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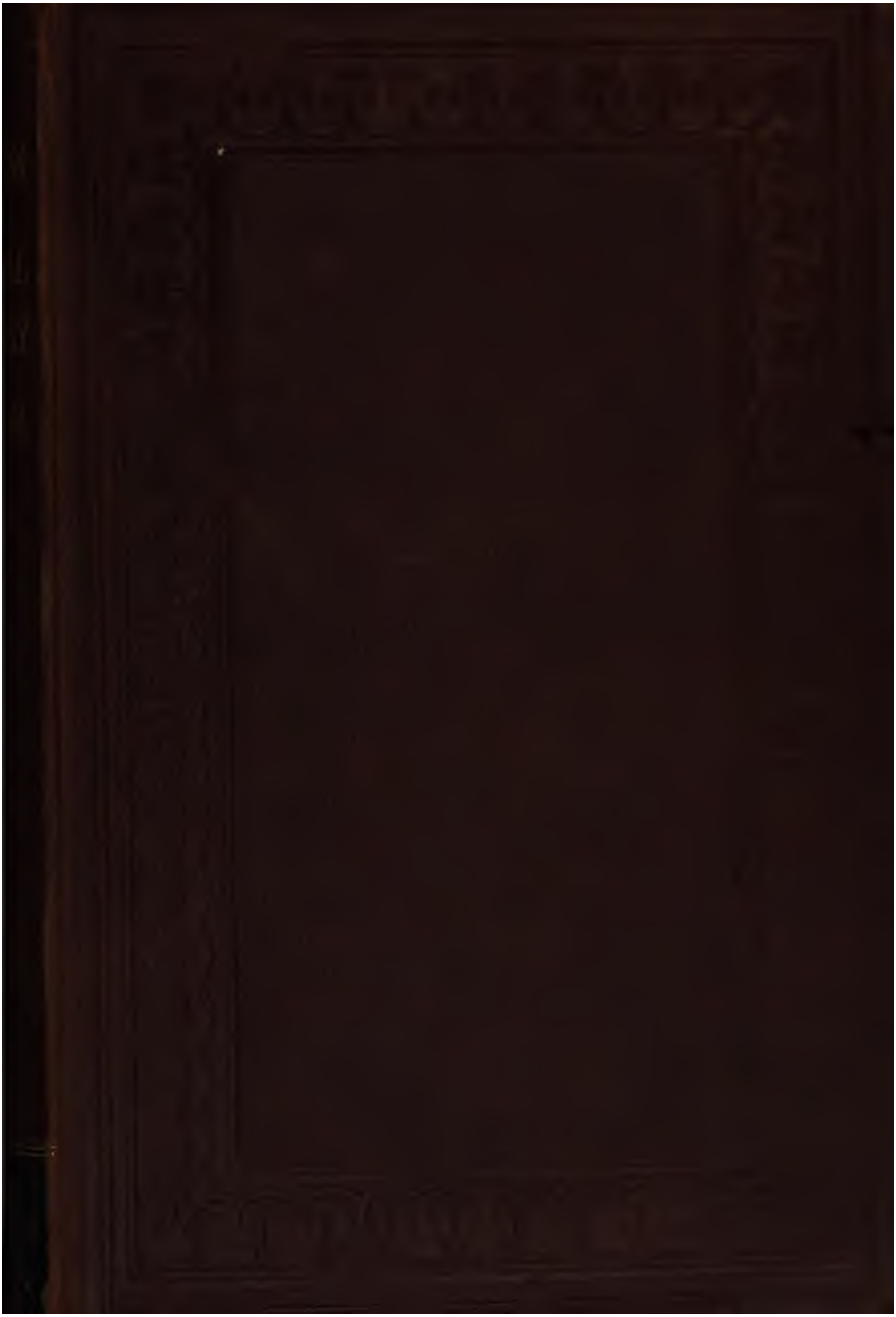

A

LABORATORY TEXT BOOK

OF

PRACTICAL CHEMISTRY;

OR,

INTRODUCTION TO QUALITATIVE ANALYSIS.

A GUIDE TO THE COURSE OF PRACTICAL INSTRUCTION GIVEN
IN THE LABORATORIES OF THE ROYAL
COLLEGE OF CHEMISTRY.

WITH 90 ENGRAVINGS.

BY WM. G. VALENTIN, F.C.S.

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PREFACE.

It is with considerable diffidence that the Author brings this text-book before the chemical public. The system of chemical notation introduced by Dr. Frankland into the lecture teaching, based upon the doctrine of atomicity, and embodied in his lucid "Lecture Notes," published four years ago, necessitated a corresponding change in the laboratory teaching. The experience gained by me during several years' teaching on this system, under comparative difficulties, owing to the want of a suitable Laboratory Text-book, has convinced me that this method of classification of elements according to their atom-fixing power, is capable of simplifying the study of chemistry generally, and in a marked degree also of chemical analysis. A knowledge of qualitative and quantitative analysis is best acquired by working practically in a laboratory. Most students can, however, devote only a limited amount of time to laboratory work; and it has, therefore, been the Author's endeavour to enter only so far into theoretical considerations as was absolutely necessary to explain the laws which govern chemical changes, and to make the beginner practically familiar with the properties of elementary matter, and the most important forms of combination met with in a limited course of practical instruction.

This has been kept strictly in view in arranging the first Part of the book. Some of the elementary exercises described therein are based upon R. Arendt's "Lehrbuch der anorganischen Chemie;" a few are borrowed from Dr. Hofmann's admirable "Introduction to Modern Chemistry."

During an extended period of laboratory teaching, I have acquired a knowledge of the difficulties usually encountered by students during their early laboratory practice; and I have endeavoured to anticipate, as far as possible, the references usually made to the teacher by students, by supplying information on points which may appear trifling, but which constitute formidable obstacles in the way of the beginner, to be cleared away only at the expense of much valuable time.

Teaching in a laboratory must be controlled by a daily examination and verification of the progress made by each student. This can obviously only be done in the case of a large practical class by expending much labour and time upon this all-important part of the laboratory work. The same question has frequently to be addressed to different students, whilst many of the latter may have to refer to the teacher on one and the same knotty point contained in the Text-book. This is an experience which other chemical instructors doubtless share with me. In order, therefore, to save time, and with a view of assisting the student, I have placed a number of questions at the end of each division of the book mostly based upon the text itself, and embodying some difficult point or other. This mode of reviewing the work done in the laboratory will, I trust, recommend itself on the important ground also of teaching a student how to prepare for examinations.

In the portion relating to qualitative analysis, it has been my chief aim to be as concise as possible, and to teach the student to generalize, and to systematize. I have frequently been told by students, with a mien of despair, "I shall never remember all these reactions!" Exercises such as the one sketched out on page 178, or the brief sketches of the different methods for the separation of the metals of the different groups, likewise the summaries of the solubility of salts under the different acids, and the table of solubility of salts given in the Appendix, will materially assist the student to remember the different and numerous reactions.

Again, in elaborating the systematic course of analysis (based mainly upon the treatises of Professors Will and Fresenius, as well as upon the "Handwoerterbuch der Chemie"), I have avoided all unnecessary innovations, and have employed only methods which have stood the test of long experience. This applies more especially to the directions laid down in the form of analytical tables for the examination of simple and complex substances. The directions given are as concise as possible, omitting everything which has no direct bearing upon the course of analysis, whilst at the same time mostly only quantitative methods have been selected.

It has been a source of great satisfaction to me, that Dr. Frankland encouraged me to write this work, and has given me in various ways much valuable assistance, for which I beg to tender him my best thanks.

I have to thank most cordially my friends, Dr. Lackersteen and Th. D. Hall, M.A., for the help cheerfully rendered to me in revising proof-sheets, and Mr. W. D. Herman, at present studying in this College, for the assistance which he gave me in compiling as complete an Index as possible.

My thanks are also due to Professor Bloxam for the loan of some of the wood-cuts used in his Treatise on "Inorganic and Organic Chemistry."

ROYAL COLLEGE OF CHEMISTRY,
London, November 21, 1870.

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PART I.

100 ELEMENTARY EXERCISES,

INTRODUCTORY TO

GENERAL CHEMISTRY,

AND TO

QUALITATIVE CHEMICAL ANALYSIS.

PART I.

CHAPTER I.

HYDROGEN.

Experiment 1.—Fill a glass cylinder or test-tube with water, and invert it over a basin containing water, by first closing its mouth with a glass plate, (Fig. 1). Wrap up a small piece of the metal sodium in a little fine wire gauze, fastened to a piece of wire. Introduce the sodium rapidly underneath the mouth of the cylinder (Fig. 2). Gas bubbles are observed to ascend through the water and to collect in the upper part of the cylinder. The evolution of gas ceases after a few moments, and the sodium is found to have disappeared entirely. By repeating this operation if necessary, the whole of the water in the cylinder may be replaced by a colourless gas. This gas is *hydrogen*.

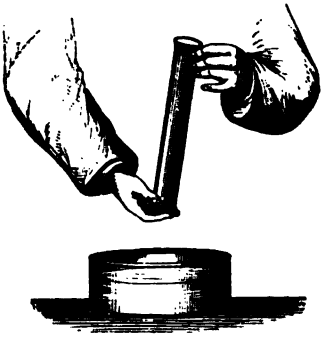

FIG. 1.

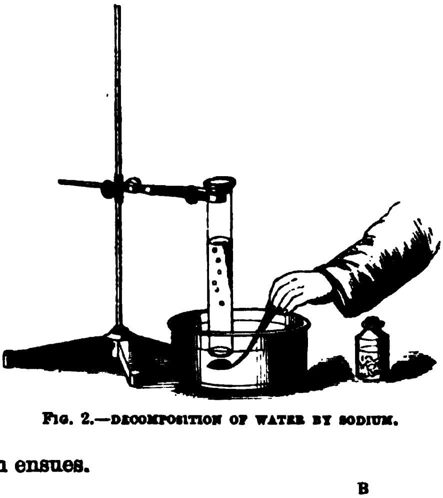

FIG. 2.—DECOMPOSITION OF WATER BY SODIUM.

Some other metals, *e.g.*, magnesium, when introduced into water, likewise give rise to an evolution of hydrogen, but the action is much slower, and has to be assisted by employing hot instead of cold water.

The metals, iron, zinc, tin, when placed in water give off no gas. If, however, a little hydrochloric acid be added to the water, a brisk evolution of hydrogen ensues.

Other metals again, such as copper, mercury, gold, and platinum, even when placed in acidulated water, do not evolve any hydrogen.

Experiment 2.—Larger quantities of hydrogen are most conveniently prepared by acting upon zinc or iron with dilute hydrochloric acid. An apparatus, represented in Fig. 3, consisting of a two-necked bottle—so-called Woulfe's bottle—is employed, fitted up by means of perforated corks with a funnel and delivery-tube. The funnel-tube, B, reaches nearly to the bottom of the Woulfe's bottle, A, and serves for the introduction of the acid. The delivery-tube, C, which has been bent as seen in Fig. 3, in the gas-flame of an ordinary fish-tail or bat's-wing gas-burner, is fitted into the other hole, so as just to pass through the cork. Sound and well-fitting corks should be selected for such experiments, and they ought to be well squeezed before being bored. The glass funnel and delivery-tube should readily pass through the holes and yet fit perfectly air tight. It is best, therefore, to bore the holes by means of a sharp cork-borer of the size of the glass tubing to be employed.

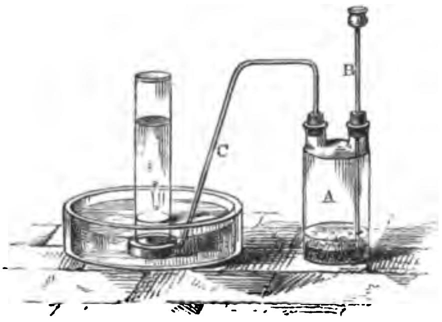

FIG. 3.—PREPARATION OF HYDROGEN FROM ZINC AND HYDROCHLORIC ACID.

The delivery-tube dips under the water and delivers the gas into the cylinder inverted over water in a basin or pneumatic trough.

Granulated zinc[*] (or strips of sheet zinc) is introduced into the bottle, and the cork and delivery-tube adjusted properly. Moderately concentrated hydrochloric acid is then poured through the funnel-tube, when the evolution of hydrogen begins at once. The gas finding no other outlet passes through the delivery-tube and forces its way through the water. The air contained in the Woulfe's bottle must first be displaced before any of the gas is collected. In order to ascertain whether the air has been sufficiently displaced, some of the gas is collected over water in a test-tube in the manner already described. When quite full, the tube is withdrawn by closing the mouth with the thumb, or with a small watch glass or glass plate. If the enclosed gas burns quietly, on applying a light to it, whilst the mouth of the tube is held downwards, with a blue lambent flame, it may be considered safe to collect the gas; but should the gas in the tube burn with a slight explosion on applying a light to it, it may be taken as an indication that the air has not been sufficiently displaced from the generating apparatus.

For storing up larger quantities of hydrogen, a gasholder, represented in Fig. 4, is usually employed, consisting of a cylindrical vessel A, made of zinc or copper, connected by means of two tubes, *a* and *b*, with the open vessel B, and supported by one or two more tubular stays, *c* and *c'*, as shown in Fig. 4; *a* and *b* can be shut off by means of stopcocks. A glass gauge, as seen in *g g'*, indicates the height of the column of water in A. By closing the opening, *d*, fitted with a screw-plug, and turning on the taps at *a* and *b*, as well as the delivery-tap at *e*, water which is poured into the vessel B makes its way into the vessel A, till it fills it entirely, and runs over through *e*. The taps at *a*, *b*, and *c* are then closed and the gas-holder may be charged with gas by inserting the delivery-tube through the opening at *d*, after the removal of the screw-plug. The water runs out from *d* as fast as the gas enters. When full, the screw-plug is replaced, and the apparatus is ready for use.

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[*] Hydrogen generated from ordinary zinc is generally contaminated with a small quantity of a most disagreeably smelling gas, whilst pure hydrogen is inodorous.

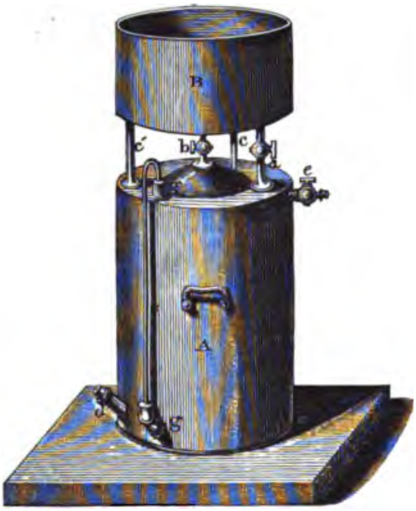

FIG. 4.—GASHOLDER.

By keeping the top vessel, B, always well supplied with water, the gas can be discharged at pleasure from A by turning on the tap *a*, which conveys the water down to the bottom of A, and opening the tap *e* partly or fully, as may be required. The water which flows from B to A presses upon the gas, and forces it from *e*. The top vessel, B, may also serve the purposes of a pneumatic trough, and gas may be filled directly from the gas-holder into an inverted cylinder by opening the tap *b*, and allowing the gas to escape through the water into the inverted cylinder.

Now, what are the properties of the gas which has been collected?

Experiment 3.—The hydrogen gas collected in a test-tube, or glass cylinder, as described in Experiments 1 and 2, can be readily removed from the basin (Fig. 5), or pneumatic trough, by closing the opening of the cylinder with the thumb or a glass plate.

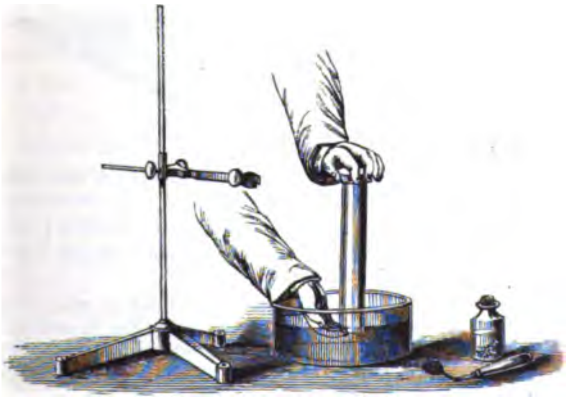
FIG. 5.

On applying a lighted candle to the mouth of the cylinder, Fig. 6, the gas burns quietly with a lambent, non-luminous flame. It is an inflammable gas.

On introducing a wax taper, as shown in Fig. 7, into the cylinder, the gas burns at the mouth quietly with a bluish flame, giving very little light, whilst the taper, on being moved upward through the flame into the hydrogen, as shown in Fig. 8, is immediately extinguished; on withdrawing the taper again, it ignites once more when it reaches the burning gas at the mouth of the cylinder. The taper may be thus extinguished and rekindled several times in succession.

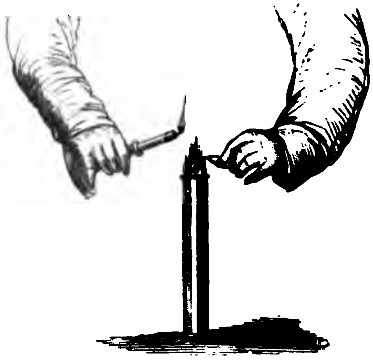

Fig. 6.

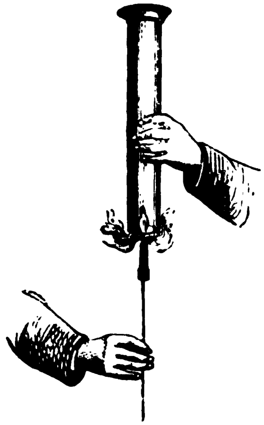

Fig. 7.

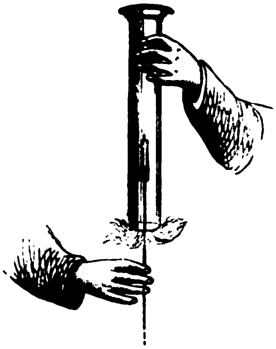

Fig. 8.

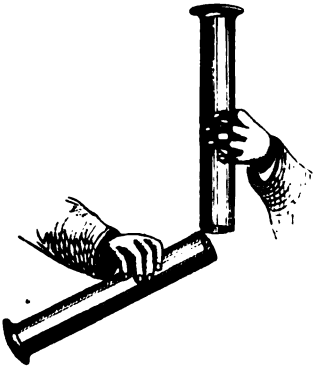

Fig. 9.

This proves *that hydrogen cannot support combustion;* also, *that it burns,* but only where it is *in contact with the air* (at the mouth of the cylinder).

Experiment 4.—A strong soda-water bottle, filled to about one-third its bulk with water, is inverted over the gas delivery tube, Fig. 3, until all the water is expelled by the bubbles of gas. A mixture of air and gas in the proportion of two to one, is thus obtained, which, when fired with a lighted taper, explodes with a loud report.

This proves *that a mixture of hydrogen gas and air explodes with violence.*

Experiment 5.—A test-tube or cylinder full of air is held, mouth downwards, and some hydrogen is allowed to pass into it from another tube, somewhat inclined, as shown in Fig. 9. On applying a light to its mouth, an explosion takes place, showing that this cylinder, which originally contained only air, contains now a mixture of hydrogen and air—a mixture which is highly explosive, as proved by Experiment 4.

This shows that the gas ascended from the lower into the upper cylinder, and that it must therefore have been *lighter than air.* Accurate determinations have established the fact, *that the gas is about* 14 *times lighter than air,* its specific gravity being ·0693, as compared with air = 1.

Experiment 6.—The delivery tube of the gas-generating apparatus is connected with a drying tube (containing calcic chloride, a substance which possesses a strong affinity for water), and a glass tube drawn out to a point (Fig. 10). After allowing the hydrogen to escape for some time, the jet may be lighted without any danger of an explosion. The gas burns with a pale blue flame, which, however, is exceedingly hot. Invert a dry bell-jar over the flame. It soon becomes covered with moisture on its inner surface, and drops of condensed water collect and run down. The same may be shown by holding a wide glass tube, about half an inch in diameter, over the jet. A musical note, high or low, according as the tube is wide or narrow, will be heard, arising from a series of small explosions, which follow one another in more or less rapid succession, as the tube is raised or lowered over the gas flame. The upper part of the tube contains the condensed water.

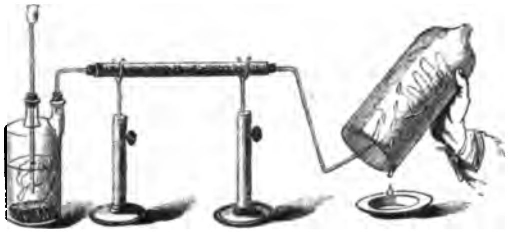

FIG. 10.

This proves *that water is formed by the combustion of hydrogen in air.* Hence the name *hydrogen* given to the gas (from ὕδωρ, water, and γεννάω, I generate), represented shortly by the symbol H.

Summary.—*Hydrogen is a very light gas. When pure it is colourless, tasteless, and inodorous.*

It is inflammable, evolving much heat, but giving little light; it does not support combustion. Water is formed by its combustion in air. Although it has no poisonous properties, it cannot support life.

CHAPTER II.

OXYGEN, NITROGEN, AIR.

Experiment 7.—Heat a little mercury nearly to boiling in a small flask (Fig. 11) provided with a long glass tube, and shake frequently. The bright metal gets slowly coated over with a reddish-yellow film, which, on shaking, adheres to the sides of the flask, and, after heating for some hours, a portion of the metal is converted into a red powder. (The vapour of the metal mercury being poisonous, care must be taken not to allow any to escape into the room through the open condensing tube.)

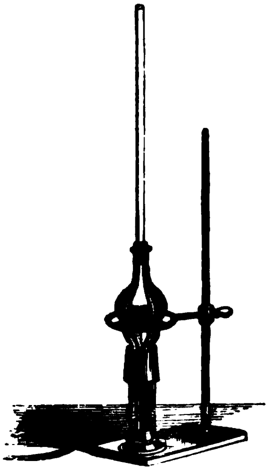
FIG. 11.—OXIDATION OF MERCURY.

On weighing the flask and metal before and after the conversion of some of the latter into the red powder, an increase in weight is observed. A ponderable substance must have been added during the heating, which can only have come from the air.

Experiment 8.—Introduce a weighed quantity of the red powder so obtained into a tube, A, of hard German glass (Fig. 12), and connect by means of a cork with a delivery tube, which dips under water in a pneumatic trough, E. On applying a strong heat to the tube in A by means of a Bunsen's gas burner, B, the air expands, and is forced out through the delivery tube. After a little time a metallic coating is observed to form in the bend, C, and gas bubbles begin to come off more briskly. Test the gas which bubbles up through the water in the pneumatic trough by bringing a glowing chip of wood near it. If the latter bursts into flame, this is due to the gas which comes off from the red powder, as air would not inflame it. A glass cylinder, D, full of water is then inverted over the mouth of the delivery-tube, and some of the gas collected. The cylinder becomes gradually filled with a colourless invisible gas. The metallic mirror in the bend of the tube increases, and collects in heavy drops. This liquid metal is mercury. When the

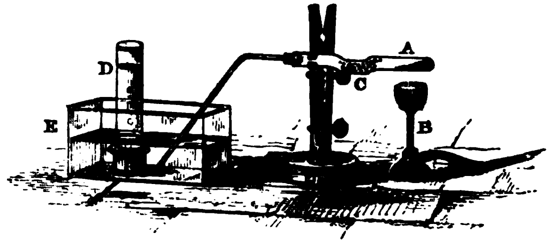

FIG. 12.—PREPARATION OF OXYGEN FROM MERCURIC OXIDE.

whole of the red powder has been volatilized, and converted by heat into a gas and a liquid metal, the lamp is removed, and the delivery-tube taken out of the water. The condensed mercury may now be weighed in a little counterpoised porcelain dish. It weighs less than the red powder employed. Something, then, has been removed from the latter, viz., the gas collected in the cylinder.

If the experiment be conducted with proper care, and in a perfectly suitable apparatus, it will be found that 100 parts by weight of the red powder leave invariably 92·59 of metallic mercury, or in the proportion of 216 : 200, and consequently yield 16 parts by weight of oxygen gas from every 216 parts of the red powder. The latter is a compound of mercury and oxygen, and is called mercuric oxide.

What is this gas, and what are its properties?

By closing the cylinder with a small glass plate, the gas can be removed without loss, and on introducing a glowing taper or ignited chip of wood into it, the taper or wood bursts into flame (Fig. 13), and burns very brilliantly.

This gas, therefore, *supports combustion* much more readily than the air from which it was originally derived (comp. Exp. 7). It is called *oxygen* from ὀξύς, sour, acid, and *γεννάω*, to generate (because chemists thought, at one time, that oxygen entered into the composition of every acid), and the symbol O has been assigned to it.

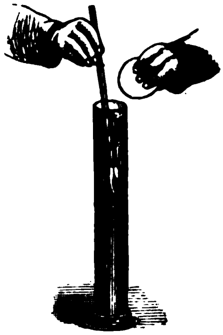
FIG. 13.

The metal mercury, symbol Hg, from *hydrargyrum*, by combining with the gas oxygen forms an *oxide*, mercuric oxide (red precipitate), and the symbol HgO, is used to express its composition.

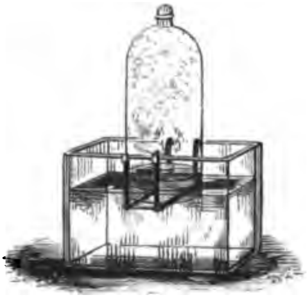
FIG. 14.—PREPARATION OF NITROGEN.

Experiment 9. — Introduce a small piece of phosphorus, dried between filter paper, into a porcelain crucible, which floats on water, as seen in Fig. 14. Set fire to the phosphorus, and rapidly invert an empty bell-jar over the burning phosphorus, so that the combustion can only take place at the expense of the air confined over water under the bell-jar. The latter becomes filled with dense white fumes, which gradually sink down, and are absorbed by the water. A diminution of about one-fifth in the volume of the air takes place, and in proportion as the air disappears, the water rises in the bell-jar. As soon as the combustion has ceased, the crucible may be removed from beneath the glass vessel. By slipping a glass plate over the mouth of the jar, it can be readily removed, and its contents examined. This is done by introducing a lighted taper into the colourless gas left in the bell-jar. The burning taper is immediately extinguished.

The gas, therefore, *no longer supports combustion. It is no longer* *air.* The phosphorus possessed a strong affinity for that constituent of the air, which is alone capable of supporting combustion, viz., the oxygen, an affinity which is greater than that which the metal mercury exhibited in the preceding experiment. The air must, therefore, be a mixture[*] of a gas which supports combustion, viz., oxygen and another gas which does not sustain combustion. This latter has been called *nitrogen*, *i.e.*, generator of nitre, also *azote* (from *a* privative, and ζωτικὸς, belonging to life).

Air, according to this approximate determination, consists of about one volume of oxygen and four volumes of nitrogen. Exact experiments have shown that air contains:—

	By volume.	By weight.
Oxygen	20·9	23·2
Nitrogen	79·1	76·8
	100·0	100·0

These proportions of oxygen and nitrogen in air have, moreover, been found to vary but little all over our globe.

The specific gravity of oxygen and nitrogen is readily deduced from these numbers, viz., $\frac{23\cdot2}{20\cdot9} = 1\cdot1$, and $\frac{76\cdot8}{79\cdot1} = \cdot97$.

Air contains, besides these two constituents, a small proportion of a gas called carbonic anhydride,[†] and more or less vapour of water.

The porcelain crucible generally contains some remnants of unburnt phosphorus, which should be kept covered with water, as the affinity which phosphorus possesses for oxygen is so great that it cannot be kept in air, and great care ought to be taken to prevent spontaneous inflammation, whilst operating with it. Phosphorus should, therefore, not be touched with the fingers, but should be taken out of the water with a pointed knife, or a pair of crucible-tongs, and cut into small pieces of the size of a pea under water.

The white fumes, or the product of the combustion of phosphorus in air, called *phosphoric anhydride*, will be explained more fully hereafter.

Experiment 10.—Expose a few thin strips of bright metallic sodium to the air in a flat porcelain dish. The metal tarnishes rapidly, and becomes coated with a dirty white layer of oxide, by abstracting oxygen from the atmosphere. The metal sodium oxidizes, in fact, slowly in air. The crust of oxide attracts moisture from the air, and speedily deliquesces. Thick pieces of metal on becoming coated over with oxide thereby become protected from the further action of dry air. On removing the layers of oxide and dissolving them in a little distilled water, a clear liquid is obtained, which feels greasy to the touch, tastes very caustic, and turns *red litmus paper blue*,[‡] *i.e.*, it has an alkaline reaction.

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[*] When a mixture of nitrogen and oxygen, in the proportions in which they are present in air, is made, no chemical combination takes place between the two gases. The mixture has all the properties of atmospheric air.

[†] This term is applied to oxides which form acids by combining with water, or salts, when added to a base. It will be explained more fully in Chapter XI.

[‡] Litmus, a vegetable colouring matter found in many lichens, is employed for preparing test-papers. The blue colouring matter is easily extracted by water

The powder is in fact an oxide of sodium, or *soda*, also called *caustic soda*, and *sodic hydrate*. The symbol for sodium is Na; from *Natrium*, the name given to the metal by German chemists.

Instead of the metal sodium we might have employed the metal potassium with similar results. An oxide of potassium, or potassa (potassic hydrate), would have been left in the dish. The symbol for potassium is K (from *Kalium*).

On account of the great attraction which these metals possess for oxygen, they have to be carefully kept in a liquid which does not contain oxygen, viz., petroleum. Sodium being so much cheaper and less oxidizable than potassium, is now almost invariably used, since it exhibits similar properties, only in a less marked degree. Sodium may be cut with a knife, and can be handled with dry fingers, without danger of its bursting into flame from too rapid oxidation. The oxides of both metals attract moisture from the air most eagerly, and are gradually converted into thick oily liquids containing sodic and potassic hydrates.

Experiment 11.—We are acquainted with other metals which are acted upon by atmospheric air. A piece of magnesium wire or foil can be kept in the air without undergoing much change. It tarnishes only slightly.

Hold the metal, however, for a moment in a flame, and it burns most brilliantly, *i.e.*, it deprives the air of one of its constituents—Oxygen, with which it forms an oxide of magnesium or magnesia. Symbol MgO. The symbol adopted for magnesium being Mg.

The wire continues to burn after its removal from the flame.

Magnesia is a white earthy-looking powder, which is but little soluble in water, has only a feebly alkaline reaction on red litmus-paper, and little attraction for water. This experiment proves that the metal magnesium has at the ordinary temperature much less affinity for oxygen than either sodium or potassium.

Metals which volatilize at a high temperature burn vividly, and with a flame, *i.e.*, in the finely divided condition of vapour they combine readily with the oxygen of the air.

Experiment 12.—Heat metallic zinc in a porcelain crucible over a gas flame (Fig. 15). It melts and becomes coated over with an iridescent film of oxide. On raising the temperature the metal volatilizes, and its fumes burst into a dazzling bluish-white flame, giving rise to white smoke of zincic oxide. Thin sheet-zinc burns in a Bunsen flame as fast as it melts. The oxide may be collected. It is not soluble in water, and shows no action upon litmus-paper.

The symbol for zinc is Zn, and for zincic oxide, ZnO.

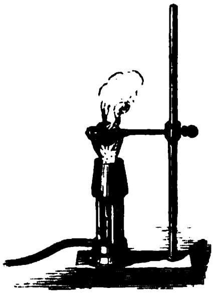

FIG. 15.—COMBUSTION OF ZINC IN AIR.

Experiment 13.—A piece of thin steel wire, when kept in dry air, remains bright and unchanged. On

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from the litmus sold in commerce—six parts of water to one part of litmus—or very dilute solution of ammonia. Sheets of unsized paper are dipped into the filtered solution and dried. To produce red litmus-paper, the aqueous solution of the colouring matter is first turned red by the addition of a few drops of very dilute sulphuric acid.

raising the temperature of the wire to intense white heat, by holding it in the flame of a gas-burner, it begins to burn, and to cast off brilliant sparks, *i.e.*, the metal iron (steel is almost pure iron) combines with the oxygen of the air *at a white heat*, and forms with it an iron oxide resembling the black iron scales that fall from a smith's anvil when a hot piece of iron is hammered out. On removing the steel wire from the gas flame, however, the combustion ceases immediately.

The symbol for this iron oxide is Fe_3O_4, the symbol for iron being Fe, from *Ferrum*. This oxide is not soluble in water, shows no alkaline reaction (in fact no reaction at all) with red litmus-paper, and is only slowly affected by water *in the presence of air* and carbonic acid being converted into *iron rust*.

These experiments prove, then, that the metal iron has less affinity for atmospheric oxygen than either sodium, magnesium, or zinc.

Experiment 14.—Heat a piece of lead in an iron spoon over a gas-burner; the metal melts, the surface of the molten metal is at first bright, then becomes covered with a yellowish film.

The oxygen of the air by combining with the lead, forms lead oxide, or plumbic oxide (from *Plumbum* lead, symbol Pb), the symbol of which is PbO. It is insoluble in water, and has no action on litmus-paper.

Experiment 15.—Heat some bright copper turnings in a gas flame, they become rapidly covered with a black film of copper or cupric oxide, CuO, (from *Cuprum*, symbol Cu), which peels off readily (copper scales), and is obtained as a black powder, insoluble in water, having no action upon litmus-papers.

The action of atmospheric air upon the metal copper may be illustrated further by a simple experiment, showing conclusively that only one constituent of the air, viz., its oxygen, is capable of combining with the copper to form the black oxide of that metal.

Experiment 16.—Fill a glass combustion tube, *e f*, with bright copper turnings, and heat the tube in a small charcoal (or, if procurable, gas) furnace (Fig. 16).

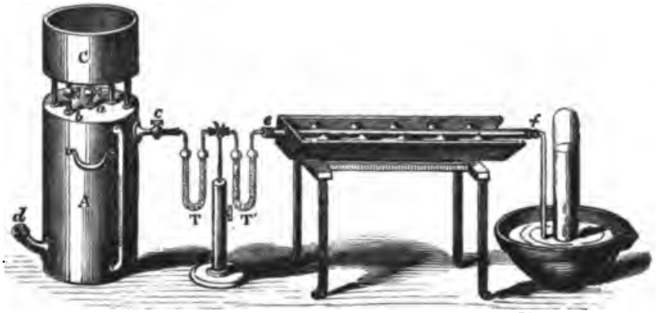

Fig. 16.—Oxidation of copper in air.

Pass a current of air from the gasholder, A. The air is made to pass through two U-tubes, T and T', before it enters the combustion-tube at *e*. The first U-tube contains small pieces of pumice-stone moistened with a solution of caustic potash, which absorbs the traces of carbonic anhydride contained in the air. The second U-tube contains pumice-stone saturated with concentrated sulphuric acid,* which possesses a powerful attraction for water, and retains every trace of moisture which the air carries along with it. Connect a delivery-tube with the end, *f*, of the combustion-tube, for the purpose of collecting the gas which passes off over a pneumatic trough, as seen in Fig. 16.

Pass air over the copper without applying heat to the tube. No action takes place, the copper retains its metallic lustre. Collect some of the air in a glass cylinder over water and introduce a lighted taper. The taper continues to burn quietly. Heat the copper next to bright redness by heaping ignited charcoal all round the combustion-tube. The metallic copper remains unchanged. Now turn on a slow current of air, and the metal is seen to blacken from the anterior end of the layer of copper turnings onwards. Collect the gas, which issues from the delivery-tube under water, in a glass cylinder, and test it again by inserting a lighted taper: it no longer supports combustion, for the taper is extinguished.

The gas is no longer air, it is in fact *nitrogen gas.*

This constitutes, then, a ready method of obtaining pure nitrogen gas.

Pass air till the whole of the metallic copper has been converted into the black oxide, which can readily be ascertained by collecting from time to time some of the gas over water, and testing it with a lighted taper. The oxidation is finished as soon as the gas supports once more the combustion of the taper.

By weighing the copper turnings previous to their introduction into the combustion-tube, and weighing again after complete oxidation has been effected, we find an increase in weight The copper, like the metal mercury in Exp. 7, has attracted some ponderable matter from the air. The increase in weight remains proportionally the same, however frequently the experiment may be repeated. The weight of the metallic copper to that of oxide is as 100 : 125·2, or (for reasons to be explained hereafter) in the proportion of 63·5 of copper to 79·5 of oxide, *i.e.*, 63·5 parts by weight of metal combine with 16 parts by weight of oxygen.

Experiment 17.—Heat gold or platinum wire, or foil, in a Bunsen gas flame. Neither of these metals is affected by the oxygen of the air.

Gold and platinum exhibit, under these circumstances, no affinity for oxygen.

Summary.—*Some metals can take Oxygen from the air and form Oxides. Combustion and oxidation are, chemically speaking, the same operation. Combustion* in air or oxygen does not imply *destruction* but merely *conversion of the combustible substance into a new body, into an Oxide.*

Some metals possess a great affinity for Oxygen, and form Oxides readily; other metals combine with Oxygen only at a high temperature; others, again, do not combine directly with Oxygen at all, possessing but a very feeble affinity for that element. These latter metals are sometimes called *noble metals.*

Atmospheric air consists mainly of two gases, of Oxygen and Nitrogen, in the proportion of about one-fifth to four-fifths by volume. Oxygen sustains combustion and animal life. Nitrogen is a non-supporter of combustion, and cannot sustain animal life.

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* The pumice-stone and sulphuric acid are heated together for a short time in a porcelain dish, and the excess of acid drained off before the U-tube is filled.

Properties of Oxygen.

Experiment 7 has shown that oxygen can be removed from atmospheric air, and obtained in a pure state. It would, however, be both expensive and tedious to obtain large quantities of oxygen by the method described. We avail ourselves in the laboratory, therefore, of the property which a certain salt, called *potassic chlorate*, possesses, of readily parting with its oxygen when heated, leaving another salt, which does not contain oxygen, viz., *potassic chloride*. This salt is as yet of interest to us only as a convenient source of oxygen.

Experiment 18.—Heat in a Florence flask or test-tube (Fig. 17) a few grammes of potassic chlorate, KO_3Cl. Collect the gas over water by means of test-tubes, or cylinders. By first powdering the salt, and then mixing a small quantity of red oxide of iron (iron rust) or black oxide of manganese with the powder, and heating such mixture in the flask, or test-tube, a far more ready evolution of oxygen is effected than by heating the salt by itself.

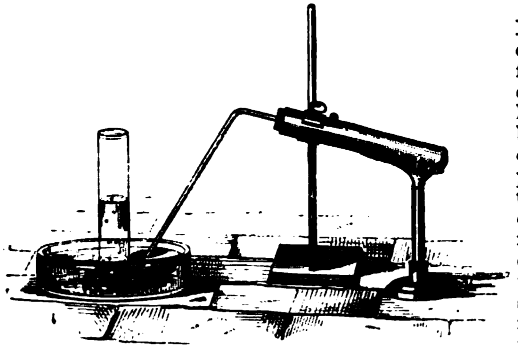

FIG. 17.—PREPARATION OF OXYGEN FROM POTASSIC CHLORATE.

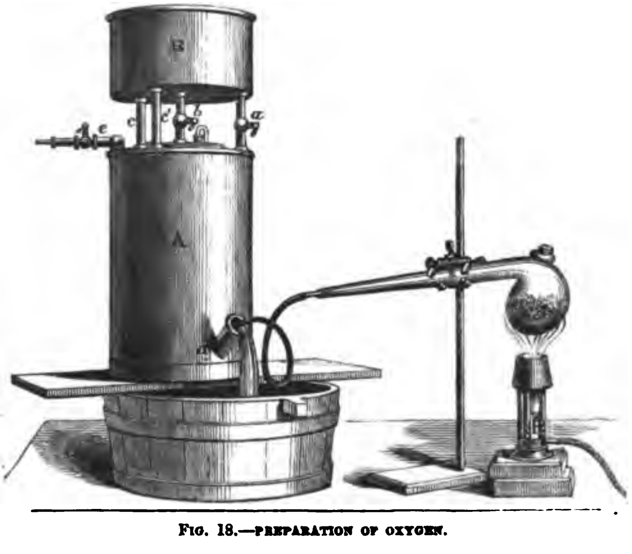

FIG. 18.—PREPARATION OF OXYGEN.

For the purpose of collecting a larger volume of gas, sufficient for several experiments, it is preferable to employ a gasholder, as shown in Fig. 18.

In order to examine the gas, it will be found most convenient to first transfer a portion from the gasholder to a tubulated bell-glass, closed by means of a cork, or a greased glass plate. The jar is completely filled under water, in the vessel B of the gasholder (Fig. 18). On placing it over the central tube, which connects the lower vessel A of the gasholder with the upper water reservoir B, and opening first the stopcock at *a*, which allows the water to flow from B to the bottom of the vessel A, and then the stopcock at *b*, the column of water in B forces the gas rapidly into the bell-jar.

In the absence of a gasholder, the gas may be directly filled into the bell-jar or cylinder, from the evolution flask or retort (Fig. 19).

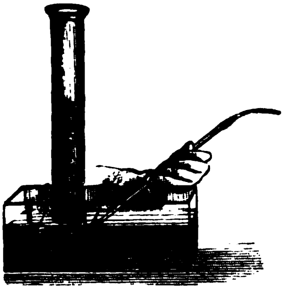
FIG. 19.

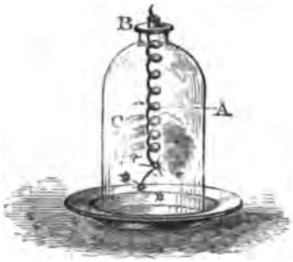

FIG. 20.

The bell-jar containing the oxygen is then removed from the water. For this purpose its wide mouth is closed under water, by dipping an earthenware plate or iron basin under it, and its contents can now be examined at pleasure.

Experiment 19.—A thin watch-spring A (Fig. 20) is fastened to a cork in the deflagrating collar B, which fits the mouth of the jar. The steel spring must be heated first, before it can be coiled up into a spiral form. In order to cause the oxygen in the jar C to act upon the iron of the watch-spring, the temperature of the latter must be raised by fastening to the end of the watch-spring a piece of tinder or dry charcoal. The tinder or charcoal is ignited, the cork or glass plate of the bell-jar is removed, and the cork with the watch-spring rapidly inserted. The tinder or charcoal, which at first only glows, burns vividly, and quickly raises the temperature of the watch-spring, till the latter burns likewise, and gives a most dazzling light, throwing off sparks of melted metal and of oxide, which fall with a hissing noise into the water of the basin below.

In place of bell-glasses, wide-necked bottles (Fig. 21) may also be employed.

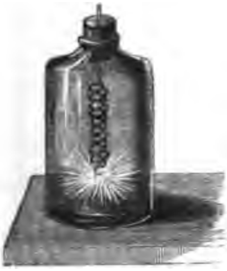
FIG. 21.

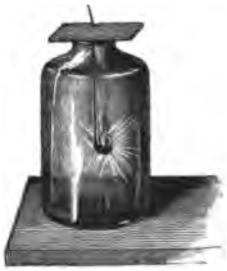
FIG. 22.

A little water ought then to be left in the bottle, sufficient to cover the bottom, and to prevent the globules of molten iron from breaking the glass.

This experiment proves that iron, which in the form of thin wire, can be burnt in air, by holding it in a gas flame, burns in free oxygen with great brilliancy, and gives off much heat. The product of its combustion in oxygen is the *iron oxide* Fe_3O_4.

Experiment 20.—Another bell-jar or bottle (Fig. 22) is filled in a similar manner with oxygen. A wooden cover is fitted to its mouth, through which passes a stout wire, to the lower end of which a small iron spoon is fastened. A few pieces of sulphur are placed in the spoon, and inflamed previous to their introduction into the oxygen gas. The sulphur burns in the air slowly, with a pale blue flame. As soon as the ignited sulphur comes in contact with the oxygen of the jar, it burns brilliantly, with a dazzling blue flame. On examining the jar after the combustion is over, a suffocating gas is found to be left, having the odour of burning matches. Introduce a piece of blue litmus-paper into the gas. It is turned red instantaneously.

The gas is called *sulphurous anhydride* (SO_2).

Experiment 21.—Fill another bottle, or bell-jar with oxygen, and introduce in like manner a piece of phosphorus, another elementary body, as we have already seen, which possesses a great affinity for oxygen. The small piece of phosphorus to be employed is dried rapidly between folds of filter-paper, and then placed in the iron spoon, ignited, and rapidly introduced into the bell-jar. Phosphorus burns with most intense light in oxygen gas, producing at the same time great heat. Should any of the burning phosphorus be spurted from the iron spoon, and come in contact with the glass, it will cause the glass to crack, without doing, however, any further harm. The whole jar is filled with clouds of a heavy white compound, which gradually subside. On letting the jar stand for a little while, these white clouds disappear. They combine with the water, with which they form an acid substance. Test the water with litmus-paper; it turns blue litmus red. The liquid possesses an acid taste.

The white compound formed by the combustion of phosphorus in oxygen gas is called *phosphoric anhydride* (P_2O_5). The product of the action of water upon this compound is called *phosphoric acid.*

Experiment 22.—Arrange apparatus in such a manner as to pass a current of oxygen gas from the delivery-tube of the gasholder over pieces of ignited charcoal placed in a piece of combustion-tube, connected by means of corks and india-rubber tubing into a glass cylinder, as shown in Fig. 23. Previous to applying heat to the charcoal, and before turning on the oxygen gas from *e*, introduce a lighted taper into the glass cylinder.

It continues to burn. Apply heat to the tube where the charcoal rests; it begins to glow. Now pass a *slow* current of oxygen gas, the charcoal immediately burns most vividly, and the combustion goes on *without any external application of heat.*

When the combustion has proceeded a few minutes, introduce the lighted taper again into the glass cylinder which received the gaseous product of combustion. The light of the taper is extinguished. The gas in the cylinder is neither air nor oxygen. A series of burning tapers fixed on wires at various heights may also be introduced into a second wider cylinder. The taper placed lowest will be extinguished first, then the next above it, and so on, till all are extinguished. The charcoal in the combustion tube is gradually consumed and carried away as gas.

It burns at the expense of the oxygen, *i.e.*, it combines with the latter and forms an oxide of carbon, called *carbonic anhydride* (CO_2).

This experiment proves then clearly that the colourless gas which results from the combustion of carbon in oxygen *does not support combustion.*

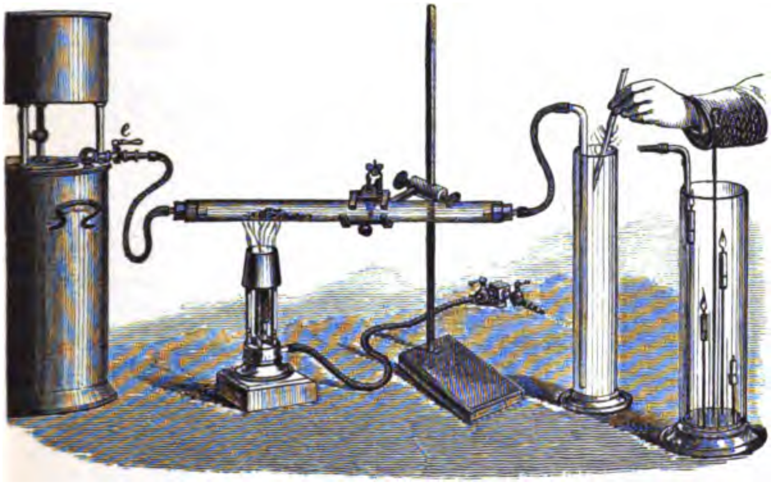

FIG. 23.—COMBUSTION OF CARBON IN OXYGEN.

Experiment 23.—Collect some of the gas in a cylinder over warm water in a pneumatic trough. Remove the cylinder when full of gas by closing it with a glass plate. Pour the gas into another cylinder in which a small burning taper is placed. The taper is extinguished, and it can be clearly seen how the carbonic anhydride by falling through the air of the upright cylinder, at first forces down the flame, till at last it entirely extinguishes it.

This proves that carbonic anhydride is *heavier than air*, and that it consequently falls through the air.

Experiment 24.—In like manner fill a stoppered glass cylinder with carbonic anhydride, close the mouth with the ground glass stopper under water, and remove the cylinder to a trough containing *cold*, but recently boiled water. Open the cylinder under water. The water rises slowly, the gas being absorbed by the water. This absorption may be accelerated by vigorously shaking. The water now tastes slightly *acid*, and a strip of blue litmus-paper is slightly reddened.

This proves that *carbonic anhydride is absorbed by water*, and *that its solution is a weak acid*, which is called *carbonic acid.* Natural waters contain carbonic acid.

Experiment 25.—Pass the carbonic anhydride generated by the combustion of charcoal in oxygen from the combustion-tube, directly into a test-tube containing lime-water (*i.e.*, a clear solution of slaked lime in water). The first bubbles cause a milkiness, and in a few minutes a quantity of a heavy white powder is formed, which on interrupting the current of gas, gradually falls to the bottom of the test-tube. This powder is evidently the result of the action of the gas upon the lime dissolved in the water. If the gas is passed somewhat longer, the white powder gradually dissolves again. This proves that the latter is soluble in excess of carbonic acid. On adding lime-water, the clear liquid becomes once more milky. The same happens when heat is applied. In the latter case some of the gas is seen to come off.

It has been already shown that water is formed by the combustion of hydrogen in air, and that a mixture of hydrogen and air, when ignited, explodes with great violence and forms water. A mixture of hydrogen and oxygen gas explodes with still greater violence, especially if the mixture consists of one volume of oxygen to two volumes of hydrogen.

The heat produced by the combustion of oxygen and hydrogen is very great. A jet of oxygen directed into a flame of hydrogen causes sufficient heat to melt a platinum wire.

Experiment 26.—Soak a good sized bladder in water till it is quite soft. Insert into the neck of the bladder V a tube provided with a stopcock *r*, shown in Fig. 24. A tubulated bell-jar is fitted with a stopcock *s*. By plunging the jar C into the water contained in the upper vessel B of the gasholder, it can be filled entirely with water by simply opening the stopcock at *s*, and allowing the air to escape. The stopcock is then shut off and the bell-jar connected with the tube of the empty bladder by means of a piece of india-rubber tubing.

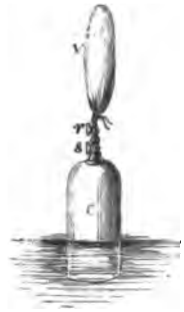

FIG. 24.

The bell-jar is next filled with oxygen, as described under Experiment 18. By opening the stopcocks *s* and *r*, the gas is transferred to the bladder V.

By filling and discharging in like manner the same bell-jar twice with hydrogen gas from another gasholder filled with hydrogen, the bladder can be charged with a mixture of one part by volume of oxygen, and two parts by volume of hydrogen. According to a beautiful law of nature, the two gases rapidly diffuse and intermingle most intimately, and the gaseous contents of the bladder now constitute a highly explosive mixture, the explosive nature of which may be shown by filling soap-bubbles with the gas. A solution of soap and glycerine is most suitable for this purpose. The cup at the upper end of the tube which delivers the gas from the bladder, is dipped into the soap-solution. The stopcock is then opened, and, by applying a gentle pressure to the bladder, a bubble can be blown and shaken off by a slight side-movement of the tube. The bubble ascends rapidly because the gaseous mixture with which it is charged is lighter than air, and can be exploded by applying a light to it as it ascends. Each bubble bursts with a sharp report.

If no gasholders are at the operator's disposal the two gases may also be filled in the proper proportions, one after another, directly from the generating flask and retort into the bell-jar, which for this purpose is divided into three equal parts, and is placed full of water over a pneumatic trough.

This experiment shows that hydrogen and oxygen do not combine at the ordinary temperature, but if the temperature of a very small portion of their mixture be raised by applying a light to it, the heat which is produced by the chemical combination of hydrogen and oxygen communicates itself with great rapidity to the rest, and the whole mixture explodes. Water is formed by the combination of two volumes of hydrogen and one volume of oxygen.

The combination of hydrogen and oxygen in these proportions can be shown in many other ways, but the highly explosive nature of the mixture renders it advisable for the operator not to attempt at first any more elaborate experiments.

Some of the elementary bodies hitherto treated of possess properties which appertain only to *metals*, others again lack such properties entirely, *e.g.*, carbon, sulphur, phosphorus. These latter bodies are called non-metals or *metalloids*.[*] Some of the elementary gases already examined, viz., oxygen, hydrogen, nitrogen, belong likewise to the non-metals.

Summary.—*Pure oxygen combines energetically with metallic as well as non-metallic elements. Oxygen mixed with nitrogen, as in air, combines less energetically. The nitrogen acts as a diluent.*

Heat is produced by the combination of oxygen with other elementary bodies. Such combination is frequently accompanied by the phenomenon of light.

The oxides of metallic bodies are solid bodies, either soluble in water and of a caustic or alkaline nature, or insoluble in water. They are also called bases.

The oxides of non-metallic bodies are either gaseous, liquid, or solid bodies. They dissolve for the most part in water, and many possess acid properties.

CHAPTER III.

CHEMICAL REACTIONS (Combinations and Decompositions). ELEMENTS.

WATER is a liquid body at the ordinary temperature. If the temperature fall below 0° Centigrade (32° Fahrenheit) this liquid solidifies and becomes *ice*.[†] Again, if the temperature of the water be raised by the application of heat, the liquid becomes converted into water vapour, or *steam*. That temperature is indicated on the thermometer scale at 100° Centigrade (212° Fahrenheit) at the ordinary atmospheric pressure. Water remains *unchanged in composition*, *i.e.*, it is still composed of hydrogen and oxygen, in the proportion by volume of two to one respectively, whether it exist in the solid, liquid, or gaseous form, as ice, water, or steam. It merely changes its state of aggregation, and this change is dependent upon a loss or gain of heat alone. It is a mere *physical* change.

The metal sodium in Experiment 1, on being brought into contact with water, decomposed it rapidly. Hydrogen gas was evolved, and the oxygen went to the metal sodium, and formed with it a new body, soda, or an oxide of sodium, differing essentially in its properties from the metal itself. Such a change is no longer a mere *physical* change, it is called a *chemical* change. A *new body was formed*, viz., soda, *by the combination of two distinctly different bodies:* the sodium, in fact, entered into chemical combination with the oxygen.

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[*] From μέταλλον, metal, and εἶδος, form. It is difficult to draw the line of demarcation between metals and metalloids very sharply. *Metals* are opaque bodies, having a peculiar lustre, known as *metallic lustre*, and are good conductors of heat and electricity. *Metalloids* do not possess these properties in the same degree.

[†] Water may be cooled to – 12° C. without freezing, if it be left perfectly undisturbed.

In Experiment 8, we saw that red oxide of mercury, when heated, gave off oxygen gas and mercury. *One uniformly constituted body thus broke up under the influence of heat, into two new bodies, differing entirely from each other.* The chemical change arose from the breaking up of one body into two. It was a *chemical decomposition* of a compound body into its constituent parts. Chemistry deals thus with *simple* bodies and *compound* bodies. A compound body which consists only of two simple bodies, is called a *binary* compound.

Water is a binary compound, and so are the metallic oxides called *bases*, *e.g.*, cupric, ferric, plumbic oxide. The names of binary compounds are constructed by using the names of the metallic element adjectively with a terminal *ic*, and giving to the non-metallic element the terminal *ide*. Carbonic anhydride is a binary compound, for Experiment 22 has shown that it is the result or *product* of the combination of the element carbon with the element oxygen. All combinations of oxygen, either with metals or non-metals, are called *oxides*, and the chemical change which gives rise to the formation of oxides, is called *oxidation*. Since at least two substances are required to produce a new body, the one acting or reacting upon the other, such chemical changes are also called *reactions*, and the bodies which act or react chemically are termed *reagents*.

By way of chemical *decomposition* simpler substances are obtained from compound bodies, as in the case of red oxide of mercury, yielding oxygen and mercury. Metals and metalloids are always simpler bodies than their oxides (bases, acids). The question naturally arises, what are the simple bodies which constitute these metals and metalloids? The answer must be, that it has hitherto been found impossible to decompose these bodies into simpler substances. Such substances, then, which cannot by any known process of decomposition in the present state of chemical knowledge be split up or decomposed into still simpler bodies, must be taken to constitute *absolutely simple* bodies. It does not, however, follow that at some future time means and ways may not be discovered, whereby these metals and non-metals may be decomposed into still simpler bodies. Such absolutely simple bodies for the time being are called *elements*. They form the basis of all chemical compounds.

The endless variety of animate and inanimate forms in nature might at first sight lead us to think that there must be an innumerable host of elements, and that to fathom them all in their manifold and varying characters must be all but impossible to the human mind. Does it not strike us, for instance, that the infinite varieties of form, colour, odour, taste, &c., which constitute the main portion of our experience as regards matter, must be due to an equally varied number of elementary constituents? And yet there are but a few elements which, by combination with each other, make up all the objects that surround us in nature—from the wonders that lie hidden beneath the surface of the earth, even to the very glories of the distant star world above. Although we are as yet very far from knowing every chemical compound that exists in nature, it may safely be stated that no element of any importance has escaped the searching eye of the chemist in that portion of our globe which is accessible to chemical investigation.

The result of such investigation has proved that only a limited number of elements exists. Up to the present time we have become acquainted with 62 elements, of which about one-half occur in nature in such small quantities, and so locally, that a limited share of usefulness only can be ascribed to them in the mineral kingdom, as well as in the economy of animate life. Others again are of the utmost importance, and appear to pervade almost every nook in nature (viz., oxygen, hydrogen, carbon, iron, aluminium, calcium, potassium, sodium). It will on this account be quite legitimate if a larger share of our attention be bestowed upon these. In the following table, arranged in alphabetical order, the 36 most important elements are distinguished by black type; those next in importance, 10 in number, by italics; whilst the rest of the elements which occur, either to a very limited extent in nature, or of which we possess as yet a very imperfect knowledge, are printed in small ordinary type. The Latin names—a few of the names are of Greek origin, but have become latinized—are given wherever the English names of elements differ therefrom. Chemists have, moreover, adopted a kind of symbolic language by writing merely, as has already been shown, in the place of the full name, the first letter of the Latin name of each element. Sometimes, for the sake of distinction, the first and second letter, or the first letter together with some leading letter out of the middle of the Latin, are used, thus Sn stands for stannum, tin; Pt stands for platinum; Pb for plumbum, lead; As for arsenic.

TABLE OF CHEMICAL ELEMENTS.

	Symbol.		Symbol.
Aluminium	Al.	**Fluorine**	F.
Antimony (Stibium)	Sb.	Glucinum	Gl.
Arsenic	As.	**Gold** (Aurum)	Au.
Barium	Ba.	**Hydrogen**	H.
Bismuth	Bi.	Indium	In.
Boron	B.	**Iodine**	I.
Bromine	Br.	Iridium	Ir.
Cadmium	Cd.	**Iron** (Ferrum)	Fe.
Caesium	Cs.	Lanthanum	La.
Calcium	Ca.	**Lead** (Plumbum)	Pb.
Carbon	C.	*Lithium*	Li.
Cerium	Ce.	**Magnesium**	Mg.
Chlorine	Cl.	**Manganese**	Mn.
Chromium	Cr.	**Mercury** (Hydrargyrum)	Hg.
Cobalt	Co.	*Molybdenum*	Mo.
Copper (Cuprum)	Cu.	**Nickel**	Ni.
Didymium	Di.	Niobium	Nb.

TABLE OF CHEMICAL ELEMENTS (*continued*).

	Symbol.
Nitrogen	N.
Osmium	Os.
Oxygen	O.
Palladium	Pd.
Phosphorus	P.
Platinum	Pt.
Potassium (Kalium)	K.
Rhodium	Rh.
Rubidium	Rb.
Ruthenium	Ru.
Selenium	Se.
Silicon (Silicium)	Si.
Silver (Argentum)	Ag.
Sodium (Natrium)	Na.
Strontium	Sr.
Sulphur	S.
Tantalum	Ta.
Tellurium	Te.
Thallium	Tl.
Thorium	Th.
Tin (Stannum)	Sn.
Titanium	Ti.
Tungsten (Wolframium)	W.
Uranium	U.
Vanadium	V.
Yttrium	Y.
Zinc	Zn.
Zirconium	Zr.

Summary.—*Changes in the mere state of aggregation of bodies are termed* **physical changes.**

Changes which give rise to a new body or bodies, differing essentially in properties from the original bodies, are called **chemical changes.** *The new body or bodies may be formed—1st. By the combination of two (or more) simple bodies, perfectly distinct in their properties; or, 2nd. By the decomposition of a compound body into two (or more) simpler bodies, differing in properties from the former.*

Bodies reacting upon each other are termed **reagents.** *The change itself is called a* **reaction.**

Bodies which cannot be decomposed by any known process into simpler bodies, differing essentially in properties, are called **simple substances** *or* **elements.**

Sixty-two elements are known up to the present time.

CHAPTER IV.

REDUCTIONS. CHEMICAL AFFINITY.

OXIDES are binary compounds. Most oxides hitherto referred to were obtained by a simple process of *addition* of element to element.

A further step towards enlarging our chemical knowledge will naturally be gained by ascertaining whether these binary compounds can be broken up into their component parts or elements; whether, in fact, the *elements contained in oxides can be isolated again.* Chemical processes of this kind are termed *reductions.*

Experiment 8 showed clearly that heat alone can split up an oxide into its two component elements, into mercury and oxygen. Reductions of so simple a nature are, however, rare; and it happens more frequently that the affinity which holds elements together in binary compounds is much greater than what we find in the case of the red oxide of mercury, and that heat alone cannot overcome it. In such a case we make use of the stronger affinity which a third element may possess for one of the elements of a binary compound.

Adhesion or cohesion exists between bodies or parts of bodies and enables them to hold together without altering their properties and to remain *what they are.* A chemical change, we have learned, produces new bodies, *different in properties* from the original bodies. Hence a chemical compound must form a far more intimate combination, and the union of the elementary component parts must necessarily extend to the smallest possible particles of the body. On this account a distinct name has been given to this uniting force, viz., *chemical affinity.* It may be defined as a *force which draws together the elements of a compound*, firmly linking particle to particle, and *which opposes itself to their separation.*

Experiment 10 has shown that sodium and potassium possess a greater liking or attraction or, as we must now call it, a greater *affinity* for oxygen than either magnesium, iron, lead, mercury, or copper. We infer therefore that it will be easier to remove the oxygen from mercuric oxide than from soda. This is actually the case, as Experiment 8 proved. If only a slight or weak affinity has to be overcome between the elements composing a binary compound, as in the case of mercuric oxide, heat alone may overcome the force which is opposed to their separation. If, on the other hand, the elements of an oxide are held together by a powerful affinity for each other inherent in each element—although heat will certainly *help* to overcome the opposition—to overcome it entirely we must call into action other elements possessing a still stronger affinity for one or other of the component elements of the oxide. Now, to discover the different degrees of affinity which different elements exhibit towards one another, and to be able to select the right element for the purpose of breaking up a binary compound, is a matter of pure experiment. Such knowledge, in fact, constitutes our chemical experience. It is possible to reason from a knowledge of well-established affinities and frequently to predict by reasoning from analogy, what changes will take place when an element acts upon a binary body. The experience gained by the few simple experiments which have hitherto been described has already taught us that potassium, sodium, and phosphorus possess great affinity for oxygen. Next to these we must classify sulphur, carbon, hydrogen, magnesium, aluminium, zinc, iron, tin, lead, copper, mercury, silver, platinum, gold; and we perceive at once why silver, platinum, and gold are noble metals, namely, because of their extremely slight affinity for oxygen.

Experiment 27.—Introduce some cupric oxide or black copper scales (see

Experiment 15) into a bulb-tube of hard glass, and pass *dry* hydrogen over it, as shown in Fig. 25. For this purpose the gas may be generated

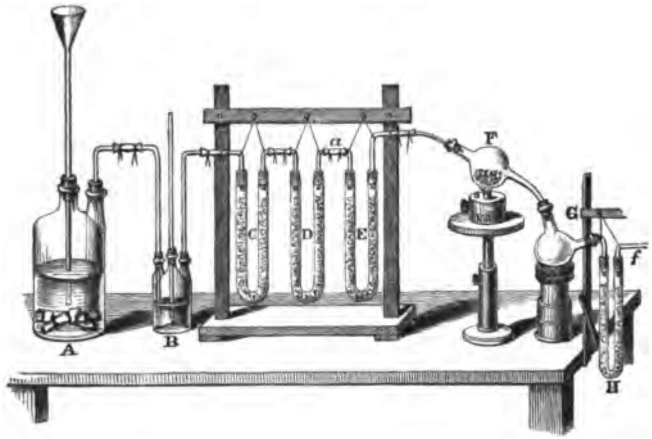

FIG. 25.—REDUCTION OF CUPRIC OXIDE IN A CURRENT OF DRY HYDROGEN.

from zinc and dilute hydrochloric acid in the Woulfe's bottle A. Commercial zinc is, however, never obtained pure, but contains invariably small quantities of carbon and sometimes of arsenic and sulphur; which form gaseous hydrogen compounds possessing a very disagreeable odour. In order to remove these impurities, the hydrogen gas is passed through a Woulfe's bottle B, containing water—a so-called wash-bottle—and then through several U-tubes, C D E, filled with small pieces of pumice-stone, before it passes over the cupric oxide in F. The pumice-stone in the first U-tube is moistened with a concentrated solution of caustic potash; that in the second with a solution of corrosive sublimate; and that in the third with concentrated sulphuric acid, which retains every trace of moisture which the gas carries with it. The cupric oxide in F is heated by a spirit lamp or gas jet; and is connected with a small two-necked receiver G, in which the greater part of the water which is produced by the deoxidation or reduction of the cupric oxide is allowed to condense, and with a U-tube H filled with pumice-stone soaked in concentrated sulphuric acid which absorbs the remaining water.

The bulb-tube is first weighed empty, then with its charge of about 4 grammes (or 60 grains) of previously ignited oxide. The difference in the weight gives the amount of cupric oxide. As soon as the air has been completely displaced from the tube, the gas which issues from the glass jet *f* may be lighted and heat applied to the cupric oxide. When the oxide has become sufficiently hot, a change is observed. It begins to glow, the hydrogen flame becomes smaller and smaller and dies out at last. Moisture condenses in the two-necked receiver G and in the U-tube H, the weight of which has been previously ascertained. If the lamp be removed from time to time the formation of steam ceases and the hydrogen can be lighted again. By continuing the application of heat, whilst passing a slow current of hydrogen, it is possible to obtain finely-divided metallic copper in the form of a red spongy powder. The experiment is continued till the whole of the oxygen of the cupric oxide has gone to the hydrogen to form water. The bulb-tube is allowed to cool in a current of dry hydrogen. It is then disconnected, the hydrogen displaced by dry air, and the bulb-tube weighed again as speedily as possible. The difference in the weight indicates the loss which the cupric oxide has suffered.

The loss is the same, however often the experiment may be repeated. It is in the proportion of 79·5 to 63·5, or, if we express it in percentage numbers, every 100 parts by weight of cupric oxide lose 20·13 of oxygen.

It is obvious that the water left in the receiver G and the U-tube H must be *the result of the oxidation of the hydrogen gas by the oxygen* removed from the cupric oxide. The increase in weight, which can readily be determined by a second weighing, consists in fact of the oxygen so removed, and the hydrogen with which it combined to form water; and for every 8 parts by weight of ponderable matter *lost* by the cupric oxide in the bulb-tube F, we find an *increase* of 9 parts by weight in the receiver G and U-tube H. We are therefore justified in concluding that *oxygen and hydrogen combine in the proportion of* 8 *to* 1 *by weight to form water.*

This experiment proves clearly that the affinity which hydrogen possesses for oxygen is not sufficient to break up cupric oxide (a binary compound) *in the cold*, but only when aided by heat. On comparing the change that took place when red mercuric oxide was heated, with the change which took place when hydrogen was passed over cupric oxide, two things become apparent, viz. :—

1st. *Both changes are reductions.*

2nd. The *second reduction is accompanied by an oxidation.*

Chemically *combined* oxygen, as well as *free* oxygen, or oxygen *mixed*, with nitrogen as in air, can therefore oxidize hydrogen and convert it into water.

It is of interest, moreover, to observe, how a gaseous body, oxygen, becomes converted into a solid by combining with copper; and on leaving the copper and combining with the gas hydrogen, is converted once more into a gaseous body, steam, which condenses into a liquid body, water.

The oxidation of the hydrogen by means of the oxygen in the cupric oxide, is termed an *indirect* oxidation.

Other metallic oxides can, in like manner, be reduced, and this process of reduction is actually resorted to when pure iron and zinc have to be prepared.

Some oxides, such as magnesia, soda, potash, cannot, however, be reduced in this simple manner. These metals have too strong a hold upon the oxygen; or, in other words, the chemical affinity which they possess for oxygen is greater than that which hydrogen possesses for oxygen, even when aided by strong heat.

From Experiment 1, we have seen that the affinity of the metal sodium for oxygen is sufficiently powerful to decompose water, *i.e.*, to deprive it of its oxygen, and thereby liberate the hydrogen in the gaseous form. The oxidation of the metal sodium was in that case likewise an indirect oxidation.

Experiment 28.—Introduce into the bulb of a hard glass tube (Fig. 26) a small piece of sodium, and pass slowly over it dry carbonic anhydride, obtained as shown in Experiment 22. No change takes place. Heat the metal contained in the bulb. It is rapidly converted into the oxide of sodium or soda at the expense of the oxygen of the carbonic anhydride, and carbon separates and remains intimately mixed up with the oxide. Allow to cool and add a little water. The soda dissolves and the carbon floats on the liquid and may be separated by filtration.

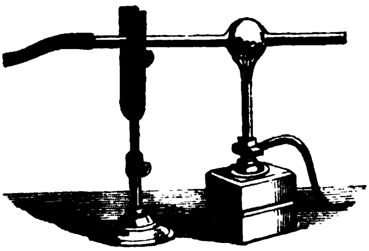

FIG. 26.—REDUCTION OF CO_2 BY SODIUM.

This experiment, viewed in connection with Experiment 22, proves that carbon can be oxidized directly by passing oxygen over charcoal heated in a tube of *hard* glass; and that the carbonic anhydride so formed can indirectly oxidize sodium, leaving free carbon.

It becomes also apparent that the metal sodium possesses a stronger chemical affinity for oxygen than the non-metal carbon; and yet sodium and potassium are obtained in the metallic state by this very action of carbon upon the oxides of these metals. Here then is an apparent contradiction.

It may be readily explained, however, if we take into account the part which heat plays in these reactions. Carbonic anhydride yields up its oxygen to the metal sodium, when the latter is gently heated, as in the preceding experiment, because *at this temperature* the affinity of the sodium for the oxygen is sufficiently excited to cause the decomposition of the carbonic anhydride. The finely-divided carbon does not, however, react upon the sodic oxide formed, the heat not being sufficient; but if a mixture of soda and carbon be exposed in an appropriate furnace, and in suitable iron vessels, to a strong heat, the affinity of the carbon for oxygen becomes stimulated to a sufficient degree to deprive the sodic oxide of its oxygen. The gaseous product of the indirect oxidation of the carbon escapes, together with the vapour of the metal sodium. The latter can be condensed into a solid body, whilst the carbonic oxide can no longer exert any action upon the metal at a low temperature.

Such chemical changes depend upon *reciprocal affinities.*

Phosphorus, we have seen, possesses, like sodium or potassium, a strong affinity for oxygen. But by mixing its oxide, phosphoric acid, or substances containing phosphoric acid, such as ground bones with charcoal, and exposing the mixture in an iron retort to a strong furnace heat, phosphorus distils off, and can be condensed in water, whilst the oxides of carbon escape as gases. It is evident then that the easy volatilization of sodium and phosphorus facilitates the process of reduction; whereas metals, such as magnesium and aluminium, which possess less affinity for oxygen, but volatilize with more difficulty than sodium or phosphorus, cannot be reduced from their oxides by the action of carbon.

Summary.—*Oxides are binary compounds, formed by the direct or indirect combination of oxygen with another element. The operation by which a compound body is resolved into its elements is called a* **reduction** (*resolution*).

The force which draws together bodies of the same or of a different chemical nature, and which opposes itself to their separation, is called **chemical affinity.**

The intensity of a chemical reaction depends upon the strength of the chemical affinity which exists between different kinds of elementary matter.

Elements which possess the greatest affinity for oxygen constitute the most powerful reducing agents.

A reduction is frequently effected by the **displacement** *(substitution) of one element in a binary body by another element.*

Such displacement depends not only upon the degree of affinity, but also upon the temperature, state of division, &c., of the bodies reacting upon each other.

Reactions are termed **reciprocal,** *when the result of one reaction constitutes the basis or starting-point of another, e.g.,*

$$\begin{aligned} AB + C &= AC + B \\ AC + B &= AB + C. \end{aligned}$$

CHAPTER V.

REDUCTION BY MEANS OF ELECTRICITY (Electrolysis).

THE reductions hitherto studied have been of a twofold nature:

1st. A simple decomposition of an oxide by heat into its component parts or elements.

2nd. A decomposition by the aid of an oxidizable body, either without heat or assisted by heat.

Electricity furnishes us with additional means of splitting up many chemical compounds into their elementary component parts. Voltaic electricity* is almost exclusively used for this purpose.

On plunging the electrodes of a voltaic battery (consisting of two zinc-carbon cells at least) into water to which a few drops of sulphuric acid have been added, decomposition of the water takes place. Oxygen escapes from the positive electrode connected with the carbon end, and hydrogen from the negative electrode connected with the zinc end of the battery. If the end of the wire of the positive electrode consists of a readily oxidizable metal, such as iron or copper, no oxygen is evolved, as the gas combines with the metal the moment it leaves the hydrogen of the water, and forms with it an oxide. Hydrogen, on the other hand, is evolved at the negative pole in the free state. In order to obtain oxygen likewise in the free state, platinum electrodes are employed, and both gases can thus be collected either separately or mixed together in the same vessel.

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* The student should study in some good manual of Natural Philosophy the laws of the electric current, and make himself familiar with the apparatus employed for producing voltaic electricity.

Experiment 29.—On introducing the platinum electrodes into water, the conductive power of which has been increased by the addition of a few drops of sulphuric acid, we observe immediately small gas bubbles forming on the strips of platinum, and escaping through the liquid (Fig. 27).

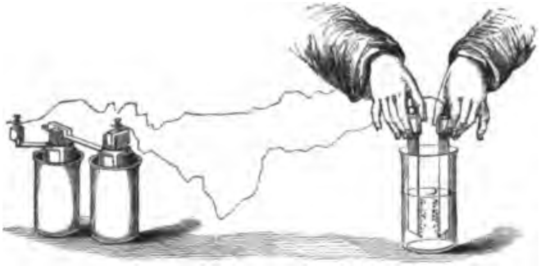

FIG. 27.

Experiment 30.—A small bottle (Fig. 28) is fitted with a cork and a short glass tube, bent at a right angle. Two platinum wires pass likewise through the cork, and end in small strips of platinum. The bottle is nearly filled with acidulated water, and the platinum electrodes are connected by means of copper wire with the voltaic battery. Gas bubbles are instantaneously seen to form on the platinum strips, and to detach themselves gradually; they rise through the liquid and escape through the delivery-tube into the cylinder, C, placed full of water over the pneumatic trough. The gas so collected detonates with great violence when a light is applied to it.

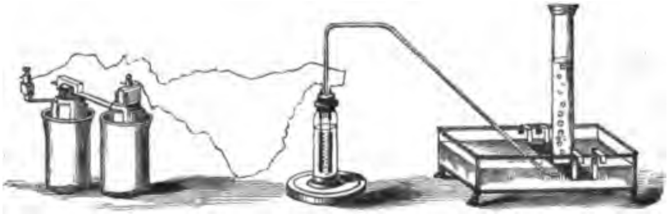

FIG. 28.

It constitutes, in fact, an explosive mixture of two volumes of hydrogen, and one volume of oxygen.

Experiment 31.—These volume proportions are shown by introducing the platinum electrodes, resting on a piece of gutta-percha, into separate cylinders of equal diameter, as shown in Fig. 29. The gas arising from the negative electrode occupies twice the space from that given off at the positive electrode. On examining the gases in the usual way, by applying a light, the larger volume of gas burns with the characteristic flame of hydrogen; the smaller volume does not burn, but supports combustion; it is oxygen gas.

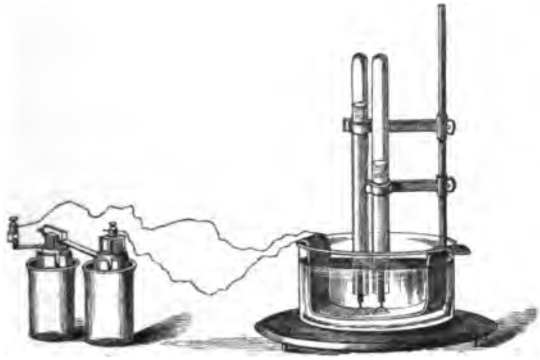

FIG. 29.

Experiment 32.—In order to show that the gases evolved at the positive and negative electrode always come off *in the proportion of one volume of oxygen to two volumes of hydrogen*, an apparatus proposed by Dr. Hofmann (Fig. 30) may be used with great advantage. It consists of a U-tube, connected from its bend with an equally wide long upright tube. The two tubes of the U-tube end in two narrow tubes, provided with glass stopcocks. The apparatus is filled with acidulated water, so that the U-tube is quite full up to the stopcocks. The main tube must be long enough to receive the liquid contained in both limbs of the U-tube. The two electrodes are introduced from below into the U-tube. On completing the circuit oxygen is seen to be evolved at the positive and hydrogen at the negative pole; the quantity of the former is, moreover, seen to be always just double that of the latter gas, however much or however little water we may decompose by the voltaic current. The gases collected in the limbs of the U-tubes are tested by opening the stopcocks, applying successively a glowing chip of wood or a lighted taper to the gas which issues from the narrow tube.

Our attention is at once fixed in the two last experiments by the *constant volume proportions* in which the two gases are obtained on electrolysing water. In fact, as often as the experiment is repeated, one volume of oxygen and two volumes of hydrogen are invariably obtained. We have, then, a right to infer that the two gases are really combined in water in these proportions.

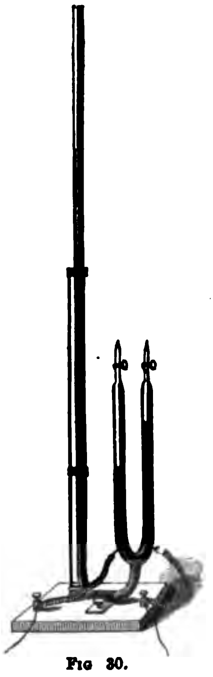

FIG 30.

Experiment 33.—It remains now only to prove that two volumes of hydrogen and one volume of oxygen, when mixed and exploded in a eudiometer-tube,* *a* (Fig. 31), combine in the very same proportions to form water. We employ for this purpose a narrow glass tube, *a*, accurately graduated for holding the explosive mixture, and place the tube in mercury contained in the glass cylinder *e*. The electric spark is made to pass between two platinum wires, fused into the upper part of the tube at *b* and *c*, which nearly touch each other within the tube, and end outside in two small loops, one of which, *b*, is connected by means of a small chain with the outer coating of a Leyden jar, charged with electricity: and by touching the other loop, *c*, with the knob of the jar, a spark passes through both platinum wires, and fires the gaseous mixture.

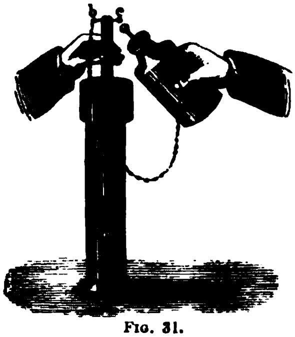

FIG. 31.

The heat which is produced by the chemical combination of the hydrogen and oxygen, momentarily expands the two gases considerably. The eudiometer should, therefore, never be more than half full of gas, and should, moreover, be pressed down firmly upon an india-rubber pad at the bottom of the mercury. As soon as it has sufficiently cooled, the steam condenses on the sides of the eudiometer, and the mercury rushes in and fills nearly the whole of the space occupied previously by the two gases.

This leads us to consider the combining relations between elementary bodies; of which, in the processes of oxidation and reduction hitherto studied, no account was taken, viz., *the quantitative proportions in which elements combine.* The combination of water by volume may be represented by the following scheme:—

$$\boxed{\mathrm{O}} + \begin{array}{c}\boxed{\mathrm{H}}\\ \boxed{\mathrm{H}}\end{array} = \boxed{\mathrm{O}\ \mathrm{H}_2}$$

The small squares are made to represent the volume units of the elementary gases; and to represent water symbolically we should write $\mathrm{O}{}^{\mathrm{H}}_{\mathrm{H}}$, or OH_2, the formation of water by the combination of oxygen and hydrogen being expressed symbolically by the equation—

$$\mathrm{O} + \mathrm{H}_2 = \mathrm{OH}_2.$$

Now if two elements such as oxygen and hydrogen are found to combine invariably *in fixed volumes*, it is clear that these two gases must also combine *in fixed proportions by weight*, for each of these gases has its own weight or specific gravity. Hydrogen has a specific gravity of 0·0693, and oxygen of 1·1056, when compared with air; hydrogen is therefore 16 times lighter than oxygen, thus:—

$$\frac{1 \cdot 1056}{0 \cdot 0693} = 16.$$

If 1 litre of hydrogen gas weighs 1, a litre of oxygen must weigh 16, and since always two parts *by volume* (2 litres) of hydrogen are required to combine with one part *by volume* (1 litre) of oxygen, two parts *by weight* of hydrogen will be necessary to combine with 16 parts *by weight* of oxygen, and in order to express symbolically the combination by volume and by weight by *one and the same scheme or formula*, water is written $O\genfrac{}{}{0pt}{}{H}{H}$, or OH_2, in which formula each H not only expresses hydrogen, but one part by weight and one part by volume, and the O not merely oxygen, the element, but 16 parts by weight and one part by volume of oxygen.

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* So called from εὐδία, calm air, and μέτρον, a measure.

Water is then composed as follows:—

By volume.	By weight.
2 vols. of H	2 parts by weight of hydrogen.
1 vol. of O	16 parts by weight of oxygen.

Or in 18 parts by weight of water (say 18lbs.) there are—

2lbs. of H, and
16lbs. of O;

and as this composition of water is constant, we can readily calculate from these figures how much hydrogen or oxygen is contained in any given quantity of water.

In order to know, *e.g.*, how much hydrogen is contained in 100lbs. of water, we have the proportion—

$$18 : 2 :: 100 : x$$
$$x = 11{\cdot}11 \text{ lbs. of hydrogen.}$$

The percentage composition (by weight) of water is therefore—

Hydrogen	11·11
Oxygen	88·89
	100·00

Now, in Experiment 27 we likewise obtained water, as the product of the reduction of cupric oxide in a current of dry hydrogen gas, and we found that the oxygen and hydrogen combined in the proportion of 8 to 1.

It is obvious, however, that the water so obtained had the same composition as the water decomposed by electrolysis in Experiment 32, and we have, therefore, no hesitation in altering the above figures to the proportion of 16 of oxygen to 2 of hydrogen, *so as to represent by the same formula, volume combination as well as combination by weight.*

Summary.—*Voltaic electricity constitutes a powerful reducing (resolving) agent.*

Gaseous elements combine in very simple definite proportions by volume and by weight. These proportions are **constant.**

Symbolic representation of chemical changes embraces by one and the same formula both volume combination and combination by weight.

Chapter VI.

CONSTANT COMBINING PROPORTIONS, ATOMS AND MOLECULES, ATOMIC AND MOLECULAR WEIGHT.

We have just established experimentally that the combination by volume of hydrogen and oxygen remains invariably the same, whether large or small volumes of the two gases enter into chemical combination, that the combining ratio of two volumes of hydrogen to one volume of oxygen gas remains in fact *constant*, and that the combining proportion by weight must, for the same reason, be likewise constant, viz., as 2 to 16.

We can conceive, moreover, that chemical combination does take place between minutely small proportions by volume of the gaseous bodies hydrogen and oxygen—between quantities far beyond the reach of experiment—and yet be convinced that all such combinations, even between the smallest imaginary gaseous particles of these elementary bodies, must take place in a like ratio of two volumes of the one to one volume of the other, and that the water so formed must possess properties perfectly identical with those observed in the water resulting from the combination of large volumes of hydrogen and oxygen. It can be proved experimentally also that when a mixture, containing an excess of either element, is exploded in a eudiometer, chemical combination takes place only so far as to satisfy the requirements of this law of definite proportions, viz., between two volumes of hydrogen and one volume of oxygen; and the portion of the element that happens to be in excess of this ratio, will remain in a free or an uncombined state mixed with the aqueous vapour. *The combining proportions remain constant.*

The composition of water by weight and by volume is capable of being demonstrated by the two methods usually pursued in chemical investigations: viz., by the *analytical** method, for we can break up water (comp. Experiment 32) into its constituent parts; and by the *synthetical*† method, for we are able to obtain water by the direct union of the two gases hydrogen and oxygen in the eudiometer tube. We have learnt to destroy water and build it up again. The means at our disposal for proving the chemical composition of water are in fact more ample than those we possess for demonstrating the constitution of most other bodies. We can break up bodies readily enough into their constituent elements, but are sometimes unable to build them up again.

If water, then, results from the chemical combination of smallest particles of two kinds of gaseous elementary matter in immutably constant proportions, it may legitimately be conceived, that chemical combination *always* takes place between such smallest particles of matter, and that every process of chemical combination between large or small bulks or volumes of gaseous matter is, in fact, merely a repetition of a process of combination between smallest possible gaseous particles or volumes; also, that chemical bodies generally consist of a number of smallest particles of matter, capable of entering into combination with smallest particles of other kinds of elementary matter.

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* From ἀνάλυσις, a loosening.

† From σύνθεσις, a putting together.

We have no conception *what* these smallest particles are, nor do we know what is their size, shape, etc. Matter itself being as yet unknown to us, need we wonder that the very existence, size, shape, etc., of the smallest particles of matter should not be capable of experimental demonstration? Where experiment fails to throw light upon the absolute nature of the constant chemical combining proportions, and can at best only supply us with relative data, hypothesis steps in.

Dalton assigned to the smallest particles of matter, between which chemical action takes place, finite proportions, and called them *atoms;*[*] assuming them to consist of the smallest particles of elementary matter which are capable of existing in *chemical combination.* According to this theory, known as the *atomic theory*, all elementary matter consists of atoms which, on entering into combination with other atoms of similar or dissimilar elementary matter, form molecules, *i. e.*, little masses from *moles*, a mass. A *molecule* of matter is the smallest quantity of a substance—elementary or compound—which is capable of existing *in the free state.*

The weight of hydrogen which combines with or is expelled from other gaseous, liquid or solid elementary matter, being relatively smaller than that of any other elementary body known to us, has, on this account, been adopted by chemists as a convenient unit or standard for determining the relative combining weights of elementary bodies. The smallest proportion by weight in which an element enters into or is expelled from a chemical compound—the smallest weight of hydrogen so entering or leaving a chemical compound being chosen as unity—constitutes the relative combining weight of such element. The observation[†] that the weight of an element in the form of gas or vapour, under like conditions of temperature and atmospheric pressure, occupies the same volume as one part by weight of hydrogen, corroborated the relative combining weight. These proportional numbers are called *atomic weights.* They are purely arbitrary numbers. The atom weight of any other element might have been chosen as the standard—in fact, oxygen at one time constituted the standard and had the combining weight 100 assigned to it—without in the least disturbing the law of constant combining proportions. By making the atomic weights of other elements the standard of comparison, as many series of atomic weights might be obtained as there are elements; and yet all would satisfy the requirements of the atomic theory, since they would all express correctly *the* **relative** *combining weights of elementary bodies.*

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[*] From ἄτομος, indivisible.

[†] Other considerations have guided chemists in the determination of atomic weights upon which we cannot, however, touch, as we lack as yet the necessary experimental data.

In water, we have already seen, there are two parts by weight of hydrogen—or as we must now call it, two atom weights—combined with 16 parts by weight or one atom weight of oxygen, the gaseous atom oxygen weighing, as we have seen, 16 times heavier than an atom of hydrogen. In like manner we have found by experiment that the metal mercury combines with oxygen in the proportion of 200 to 16 and we have no hesitation to assign to the metal mercury the atomic weight 200: that is to say, one atom of mercury, weighing 200, by combining with one atom of oxygen, to form 216 parts by weight of mercuric oxide, takes the place of two atoms of hydrogen in water. Copper, we have seen, combines with oxygen (compare Experiment 27). The increase in weight was invariably as 63·5 of copper to 79·5 of the oxide. The atomic weight of copper must therefore be 63·5; *i.e.*, one atom of the element copper, weighing 63·5, entered into combination with 16 parts by weight of oxygen and replaced two atoms of hydrogen in water.

It is obvious that we should have no difficulty in fixing the atom weight of copper if this elementary body could be obtained like hydrogen in the gaseous condition. We should simply have to determine the specific gravity of a given volume, say one litre of gaseous copper, and divide the weight of such volume by the weight of an equal volume of hydrogen. We should next have to double the number so obtained, because the atom copper takes the place of no less than two atoms of hydrogen. We can conceive, however, that the oxygen gas which existed in a solid condition in combination with the metal copper, and which was removed in Experiment 27 by the action of the gaseous hydrogen in the form of water, leaving behind solid metallic copper, was attacked by one hydrogen atom after another, and that for every two atoms of hydrogen, with which an atom of oxygen combined, one atom or 63·5 parts by weight of copper were set free, so as to leave for every 79·5 parts by weight of cupric oxide which were acted upon, 63·5 parts by weight of metallic copper, and 18 parts by weight of water. If, then, combination between smallest particles by weight of oxygen and hydrogen can be conceived, it is equally conceivable that smallest particles (or atoms) of the solid body copper were combined with smallest particles (or atoms) of oxygen, and that the binary compound cupric oxide consisted likewise of smallest particles (or atoms) of copper and oxygen, combined in immutably constant proportions by weight.

Now, in anticipation of experimental confirmation, we may say that the same holds good for other elements. The atomic weights were found to differ for every element, and had to be determined in every single case by experiment. Such quantitative experiments are among the most difficult and delicate chemical operations; let it suffice, then, to remark that the law of combination according to constant proportions by weight and by volume, has been established experimentally with the utmost precision, and that we shall have frequent opportunity, as we enlarge our knowledge of chemical compounds, to satisfy ourselves of its perfect consistency.

The symbols which have hitherto merely represented the individual elements gain thus in interest, since they not only recall the *name* of the element, but indicate at the same time *one atom* of such element, together with its particular *combining weight* and, with few exceptions, its *combining volume*.

The following tables give the names, symbols, and atomic weights of the 36 most important elements:—

NON-METALLIC ELEMENTS (*Metalloids*).

Oxygen	O	16	Nitrogen	N	14
Sulphur	S	32	Phosphorus	P	31
Chlorine	Cl	35·5	Carbon	C	12
Bromine	Br	80	Boron	B	11
Iodine	I	127	Silicon	Si	28·5
Fluorine	F	19			
			Hydrogen	H	1

METALLIC ELEMENTS.

Light Metals:			**Heavy[*] Metals:**		
Potassium	K	39	Chromium	Cr	52·5
Sodium	Na	23	Iron	Fe	56
			Zinc	Zn	65
Magnesium	Mg	24	Manganese	Mn	55
			Cobalt	Co	58·8
Barium	Ba	137	Nickel	Ni	58·8
Strontium	Sr	87·5			
Calcium	Ca	40	Tin	Sn	118
			Gold	Au	196·7
Aluminium	Al	27·5	Platinum	Pt	197·4
			Lead	Pb	207
			Mercury	Hg	200
			Silver	Ag	108
			Copper	Cu	63·5
			Cadmium	Cd	112
			Bismuth	Bi	208
			Arsenic	As	75
			Antimony	Sb	122

Combination by volume, we have seen, takes place in accordance with the law of constant combining proportions by weight; *i.e.*, two volumes of hydrogen will invariably combine with one volume of oxygen to form water (steam).

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[*] The metals which possess a higher specific gravity than 5, and which are not acted upon, at the ordinary temperature, by the oxygen of the air, are called heavy metals.

What volume, however, does the steam so formed occupy? This question can only be answered experimentally.

In order to measure the volume of steam left in the eudiometer-tube (Experiment 33), hydrogen and oxygen gases must be exploded at a temperature at which the steam produced cannot condense. Dr. Hofmann has devised an apparatus* which accomplishes this in a very elegant manner.

Experiment 34.—A mixture of two volumes of hydrogen and one volume of oxygen is introduced into a U-tube (Fig. 32), the eudiometer-tube is, however, surrounded by a jacket consisting of a wider glass tube fixed over it air tight by means of corks. The vapour of amylic alcohol, a liquid boiling at 132° C., is made to pass through the intervening space, and the gaseous mixture acquires thus rapidly a temperature of 132° C. It is then exploded in the usual manner. The two gases combine and form water, which remains, however, as steam, and is found when the pressure in the two limbs of the apparatus is equalized, to occupy only two-thirds of the volume which the mixture of hydrogen and oxygen occupied before explosion.

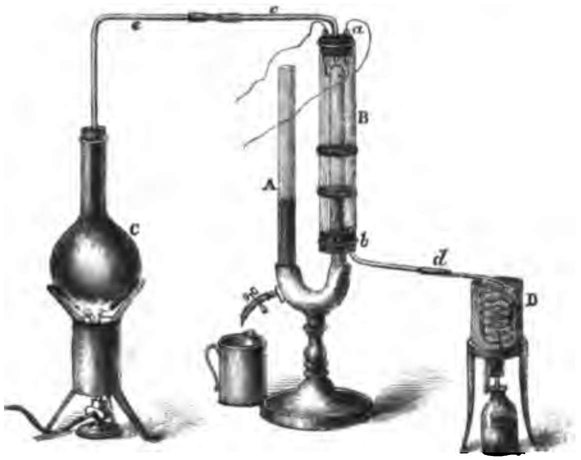

FIG. 32.—VOLUMETRICAL COMPOSITION OF STEAM (HOFMANN).

Consequently three volumes of gas contract into two volumes.

$$\boxed{\mathrm{O}} + \begin{array}{c}\boxed{\mathrm{H}}\\ \boxed{\mathrm{H}}\end{array} = \boxed{\mathrm{O}\quad \mathrm{H}_2}$$

A molecule of steam occupying two volumes is, therefore, made up of two volumes of hydrogen and one volume of oxygen, and the weight of one volume of steam must be the weight of one volume of hydrogen and half a volume of oxygen, or 1 + 8 = 9. The specific gravity of steam is therefore 9; *i.e.*, one litre of steam is nine times as heavy as one litre of hydrogen gas—the unit of comparison adopted for gas volumes—and its actual weight will be found by multiplying the weight* of a litre of hydrogen ·0896 grm. by 9

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* Modern Chemistry, page 53.

$$\cdot 0896 \times 9 = \cdot 8064 \text{ grm.}$$

A similar contraction of volume frequently takes place, when other gaseous mixtures combine chemically; the resulting gaseous volumes are (with a few exceptions) two-volume vapours.

Compound bodies can have no atom volume, they possess only molecular volumes. Hence if we wish to compare gaseous elements and compounds with each other, we have to adopt molecular weights, both for elements and compounds, as the measure of the combining quantities. Thus, in order to compare the volume of the element hydrogen with the gaseous compound body, steam, we have to compare the molecular volume of hydrogen with the molecular volume of steam—

$$\boxed{H\quad H} \quad \text{and} \quad \boxed{O\quad H_2}$$

Other reasons, also, to which we cannot refer here, render it desirable that hydrogen, when regarded in relation to other gaseous bodies, should be expressed as the molecule H H, or H_2, and not as H, the atom. The same applies to other gaseous elements. Since the volume of a gas varies with the pressure of the atmosphere and the temperature, these molecular gas volumes would necessarily be of variable dimensions, a conception which runs counter to the idea we have formed of the constitution of atoms and molecules. All gases expand, however, under the influence of heat in the same ratio. For every degree of the centigrade thermometer scale above 0° C., they expand ·3665 per cent., or, less accurately $\frac{1}{273}$ part of their bulk at 0°. The average weight of the atmosphere at the level of the sea is that of a column of mercury 760 millimetres† high. Now, according to the law of Boyle and Marriotte, the volume of a gas is inversely, and its density directly as the pressure which it sustains if the temperature remain constant. We have, therefore, no difficulty in reducing gases to the standard agreed upon by chemists, viz., a temperature of 0° C. and 760 mm. atmospheric pressure, at whatever temperature or barometrical pressure they may have been measured.

EXAMPLE.—A gas volume, say 100 cubic centimetres, was measured when the temperature of the gas was 15° C., and the atmospheric pressure 770 mm. What volume will the gas occupy at 0° C. and 760 mm. pressure?

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* Dr. Hofmann assigned the name *crith* (from κριθή, a barleycorn) to the weight of 1 litre of hydrogen, ·0896 grm. at 0° C., and 760 mm. barometrical pressure.

† The student should make himself familiar with French weights and measures. (See tables in Appendix.)

Correction for temperature—

1cc. at 0° expands into 1 + (15 × ·003665) at 15° C.
1·054975 : 1 :: 100 : x x = 94·7889 cc.

Correction for pressure—

760 : 770 :: 94·7889 : x. Ans. = 96·0360 cc.

Multiple Proportions.—If the conception which we have acquired of atoms be correct, it follows of necessity that only *whole* or undivided atoms can combine with each other. There is no reason, however, why *several* atoms of one element should not be capable of entering into combination with one or several atoms of another element to form a new compound.

With the experimental data which are at present at our command, we must content ourselves with merely stating that sulphur and oxygen combine in the proportion of one atom of sulphur to two atoms of oxygen to form sulphurous anhydride, SO_2 (Experiment 20), two atoms of phosphorus with five atoms of oxygen to form phosphoric anhydride, P_2O_5 (Experiment 21), carbon with two atoms of oxygen to form carbonic anhydride, CO_2 (Experiment 22), and we shall hereafter have to consider many more instances of combination in multiple proportions of a similar nature. We shall also shortly learn that sulphur can combine with three atoms of oxygen, and carbon with one atom as well as with two, that in fact several combinations are possible between two elements, without prejudice to the law of constant combining proportions by weight.

There exist scarcely any chemical elements between which at least two combinations could not take place, whilst there are many elements which can combine with others in three, four, five, and more proportions. As the number of atoms accumulates in a compound, its molecular structure becomes more and more complex, but the combining proportions by weight and by volume stand in a simple ratio to one another, and will be invariably multiples of the simpler combining proportions.

Summary.—Law of Constant Combining Proportions. - *All elements combine according to constant proportions by weight. The numbers which express the respective weights of the elements so combining are* **proportional** *numbers. The* **unit of comparison** *accepted by chemists is the weight of* **hydrogen,** *on account of its being less than that of any other element.*

The smallest proportion by weight in which an element enters into or is expelled from a chemical compound constitutes its **atomic weight,** *the weight of hydrogen being taken as unity.*

An **atom** *is the smallest particle of matter capable of entering into, or existing* **in a state of chemical combination.**

A **molecule** *is the smallest particle of matter capable of existing* **in the free state.**

A molecule consists, except in a few cases, of at least two atoms. The atoms of each kind of isolated elementary matter exist, with few exceptions, in combination with each other or are associated in pairs, and constitute then an **elementary molecule.**

The **molecular weight** *of a compound is, with few exceptions, identical with its atomic weight.*

The **molecular volume** *of a compound equals, with very few exceptions, the molecular volume of hydrogen at the same temperature and pressure.*

Hence the law :—**Equal volumes of all gases and vapours contain at the same temperature and pressure an equal number of molecules,** *and the molecules of all compounds in the gaseous or vaporous condition, no matter how great may be the aggregate volume of their constituents, occupy, with very few exceptions, one uniform volume, when compared at the same temperature and pressure, viz., that of two volumes, or one molecule of hydrogen.*

Law of Multiple Proportions.—*When two elements combine with each other in more than one proportion, the quantities by weight of the one element, which combine with a constant quantity of the other, are invariably integer multiples of its smallest combining quantity.*

CHAPTER VII.

SULPHUR—Its Properties.—SULPHIDES.

OXYGEN is one of the most widely diffused elements in nature; it forms a most important constituent of a great portion of inorganic or mineral nature, and is likewise of paramount importance in the animal and vegetable economy. We have seen that it combines chemically with other elements—often with great energy—and that it forms compounds of a *well defined* chemical character.

No other element equals oxygen in this respect. Many, especially the metals, possess only a limited combining power, and among the metalloids there are only two, sulphur and chlorine, which, if we merely consider their power of forming well characterized inorganic chemical compounds with other elements, are of like importance.

Sulphur is at the ordinary temperature a solid body of yellow colour. In commerce it is commonly obtained in the form of *flowers of sulphur* or *roll sulphur* (brimstone).

Experiment 35.—Flowers of sulphur can be heated over boiling water in an open vessel, *e.g.*, a porcelain dish, without melting, it merely agglutinates; at 111·5° C., however, it melts to a honey-like liquid, on heating somewhat more strongly (to 250° or 260° C.) the colour changes to red brown, almost black, and the liquid becomes very viscid, so that the open vessel may be turned upside down without any of the liquid sulphur running out. If sulphur be heated in a retort (Fig. 33), the same changes will be observed, and if the application of heat be continued longer no further change of colour is seen, but the sulphur becomes less viscid, and begins to sublime, and at about 440° C. it boils and distils. The liquid sulphur is allowed to drop into water. The strings of distilled sulphur remain for several days quite soft and elastic.

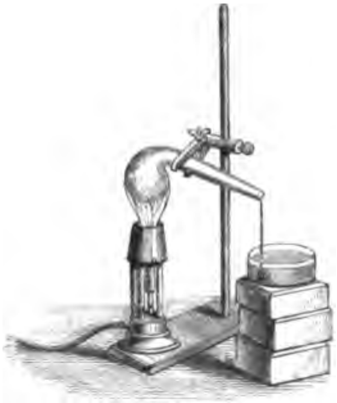

FIG. 33.—DISTILLATION OF SULPHUR.

Sulphur occurs in nature more or less pure in the free state, particularly in volcanic regions, *e.g.*, in Sicily and other places. It may be purified by *distillation** from any mineral non-volatile ingredients with which it occurs mechanically mixed. By far the greater quantity of sulphur is, however, found in nature in the *combined* state, especially with metals (as blende and pyrites) and with oxygen and metals (as metallic sulphates).

Heated in air, or in oxygen gas, sulphur bursts into flame at about 270° C., and burns with a pale blue, slightly luminous flame, forming sulphurous anhydride (comp. Exp. 20), which is readily recognized by its odour. One atom of sulphur combines invariably with two atoms of oxygen. The change may be expressed symbolically—

$$S + O_2 = SO_2,$$

i.e., 32 by weight of sulphur combine with 2 × 16 = 32 by weight of oxygen to form 64 by weight of sulphurous anhydride. It may be instructive to prove synthetically by a simple experiment the volume composition of sulphurous anhydride.

Experiment 36.—Fill a glass flask, best a litre flask (Fig. 34), over mercury, with dry oxygen gas. Introduce a piece of sulphur, placed on a small iron cup fastened to an iron wire, and ignite the sulphur within the flask by means of a concave mirror and sunlight. The sulphur can only burn at the expense of the oxygen. It forms, as we already

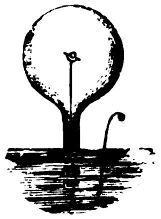

FIG. 34.—VOLUMETRICAL COMPOSITION OF SO_2.

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* This chemical operation effects the separation of a volatile from a less volatile or fixed body. The distilling apparatus must be provided with a *condenser* if the substance becomes vaporized at a low temperature. The product of the distillation, called *distillate*, is collected in a receiver.

know, sulphurous anhydride. The bulk or volume in the flask remained the same—no expansion or contraction took place.

This proves that sulphurous anhydride contains its own bulk of oxygen.

Now the weight of sulphurous anhydride gas compared with atmospheric air has been carefully determined. It is 2·247, air being 1. If we deduct, therefore, from the weight of one volume of the gas (represented by the number which expresses its specific gravity compared with air, viz., 2·247), the weight of its own bulk of oxygen (density 1·106), we must obviously get the weight of the sulphur contained in the same volume of sulphurous anhydride—

Weight of one volume of sulphurous anhydride	2·247
„ „ oxygen	1·106
	1·141

A figure which pretty closely expresses the weight of ½ volume of sulphur vapour (the specific gravity of gaseous sulphur being 2·21, as compared with air), viz., $\frac{2\cdot21}{2} = 1\cdot105$.

Half a volume of sulphur vapour cannot, however, enter into chemical combination, any more than half atoms can exist; and we get, therefore, by doubling the volume proportions—

1 volume of sulphur vapour and
2 volumes of oxygen gas;

which we may express thus—

$$\boxed{\mathrm{S}} + \begin{array}{c}\boxed{\mathrm{O}}\\ \boxed{\mathrm{O}}\end{array} = \boxed{\mathrm{S}\quad \mathrm{O_2}}$$

The molecular weight of SO_2 is $32 + 16 \times 2 = 64$ and 1 litre must weigh 32 times as heavy as 1 litre of hydrogen or $32 \times {\cdot}0896$ grm. = 2·8672 grms.

Nearly all metals are capable of uniting directly with sulphur, when heated with it, or when the vapour of sulphur is passed over the ignited metal. The metal mercury alone combines with sulphur in the cold, on account of its being a liquid at the ordinary temperature.

Sulphur forms with Metals Sulphides.

Experiment 37.—*Cupric sulphide* may be formed by heating together sulphur and copper turnings in a flask (Fig. 35). The sulphide so obtained is a black hard substance insoluble in water—

$$Cu + S = CuS.$$

Native copper sulphides are found in Cornwall and other places.

Experiment 38.—Heat in a test-tube (Fig. 36) a little sulphur till the sulphur vapour fills the greater part of the tube, then introduce finely-granulated lead or tin, in small quantities at a time, and heat it still more. Combination between the metal and the sulphur takes place. A sulphide of lead or tin is formed according to the equations:—

$$Pb + S = PbS$$
$$Sn + S_2 = SnS_2,$$

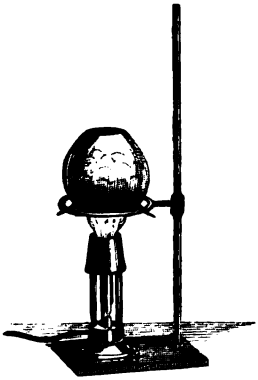

FIG. 35.—PREPARATION OF CUPRIC SULPHIDE.

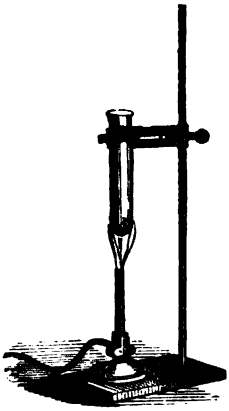

FIG. 36.—PREPARATION OF STANNOUS SULPHIDE.

the plumbic sulphide being left as a non-crystalline, dull-black mass; the stannous sulphide as a greyish black mass.

Lead is found in nature chiefly in combination with sulphur as *Galena*, PbS. Tin occurs most frequently as oxide, but likewise as sulphide (together with copper, iron, and zinc).

Experiment 39.—A thin plate of wrought-iron (not cast-iron) is heated over a Bunsen lamp to white heat, and the heated part rubbed over with a piece of roll-sulphur. Combination between the metal and the sulphur takes place. A ferrous sulphide peels off, and the plate appears as if burnt through. The sulphide is black and insoluble in water—

$$Fe + S = FeS.$$

The natural compounds of sulphur and iron, such as *iron pyrites*, are of considerable interest.

Experiment 40.—When iron pyrites, FeS_2, is heated in a test-tube or a piece of combustion-tube closed at one end, out of contact with the air, it parts with one-third of its sulphur. The change is expressed by the equation—

$$3FeS_2 = S_2 + Fe_3S_4.$$

The sulphur sublimes and condenses in the upper part of the test-tube or ignition-tube, in orange-coloured drops, which solidify on cooling into yellow masses of solid sulphur.

Experiment 41.—One part by weight of sulphur and about six parts by weight of mercury (*i.e.*, atomic weights of sulphur = 32 and of mercury = 200) are rubbed together in a mortar. The little globules of mercury gradually disappear and a black powder is obtained. A partial combination takes place when the mercury and sulphur are rubbed together for several hours. As rubbing alone cannot, however, unite mercury and sulphur thoroughly, the black mass is cautiously heated in a porcelain dish or crucible, when further chemical combination takes place with slight explosions, a clear instance of the difference between mere mechanical mixture and chemical combination. Mercury and sulphur form mercuric sulphide. A similar reaction takes place when sulphur is melted, and five to six times its weight of mercury gradually stirred into it, till the sulphur begins to get viscid. Combination takes place accompanied by a flash of light and a slight report, and not unfrequently some of the mixture is violently ejected from the crucible. The mass which is left is dark red. When cold it may be pulverized, and on mixing it with a little sulphur and heating in a flask with a long neck loosely closed with a conical piece of charcoal, the mercuric sulphide sublimes as a fine red powder, called *cinnabar*.

Cinnabar is also found as a mineral. It is insoluble in water.

Sulphur combines likewise with Metalloids.

The compound which it forms when burning in air or oxygen, *viz.*, sulphurous anhydride gas, has already been noticed. Another gaseous compound of sulphur is of great importance, *viz.*, the compound which it forms with hydrogen, called sulphuretted hydrogen, or hydric sulphide. These two elements combine directly with each other; but only under exceptional conditions.

Experiment 42.—Treat some ferrous sulphide[*]—(or any other sulphide of the same group of metals,)—with dilute hydrochloric acid or sulphuric acid in a generating flask (Fig. 37). A colourless gas is evolved possessing a most fœtid odour—

$$FeS + 2HCl = FeCl_2 + SH_2.$$

Sulphuretted hydrogen may be collected over tepid water. It is a combustible gas, for as soon as a lighted taper is brought into contact with it, the gas bursts into flame and burns (where it is in contact with the air) with a fine blue flame. The hydrogen is burnt or oxidized into water—

$$O + H_2 = OH_2,$$

and the sulphur into sulphurous acid gas—

$$S + O_2 = SO_2,$$

the presence of which makes itself rapidly perceptible by its pungent and suffocating odour.

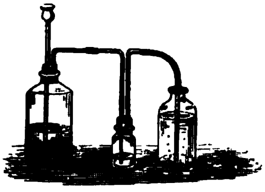

FIG. 37.—PREPARATION OF SULPHURETTED HYDROGEN.

When sulphuretted hydrogen is inhaled in somewhat large quantities it acts like a poison. Small animals die in an atmosphere containing as little as $\frac{1}{1000}$ to $\frac{1}{1500}$ of this poisonous gas. It is found wherever decomposition of organic compounds containing sulphur takes place, *e.g.*, in sewers. Cold water absorbs from 3 to 4 times its volume of this gas; and a solution of sulphuretted hydrogen in water forms one of the most important reagents in the laboratory. It is, however, rapidly decomposed when left in contact with air, finely divided white sulphur being precipitated.

If we examine into the combination by volume which took place

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[*] Native iron pyrites (FeS_2) cannot be employed, because it is not acted upon by dilute hydrochloric or sulphuric acid. The ferrous sulphide (FeS) is prepared by fusing in a Hessian crucible, heated in a fire, a mixture of 7 parts of iron filings or turnings and 4 parts of sulphur (*i.e.*, atomic weights of iron = 56 and sulphur = 32).

between sulphur and hydrogen, we have no difficulty in recognising a resemblance between the constitution of water, OH_2, and that of sulphuretted hydrogen, SH_2. The latter gas may in fact be viewed as sulphur water, or water in which the atom (or volume) of oxygen has been replaced by an atom (or volume) of sulphur.

$$\boxed{O} + \begin{matrix}\boxed{H}\\\boxed{H}\end{matrix} = \boxed{O \quad H_2} \qquad \boxed{S} + \begin{matrix}\boxed{H}\\\boxed{H}\end{matrix} = \boxed{S \quad H_2}$$

Its molecular weight is $32 + 2 = 34$. One litre of sulphuretted hydrogen compared with the volume unit (one litre of hydrogen) weighs 17 times as much, or $17 \times \cdot 0896 = 1 \cdot 5232$ grm. The specific gravity of sulphuretted hydrogen compared with hydrogen is therefore 17, and when compared with air 1·199.

The great affinity which metals possess for sulphur enables us to separate most metals from their saline solutions in the form of sulphides.

Experiment 43.—Dissolve a few crystals of the following well-known salts in distilled water (solutions 2 and 3, with the addition of a little ammonia), and pass sulphuretted hydrogen gas through their solutions, using test-tubes or bottles fitted with doubly-perforated corks (Fig. 38).

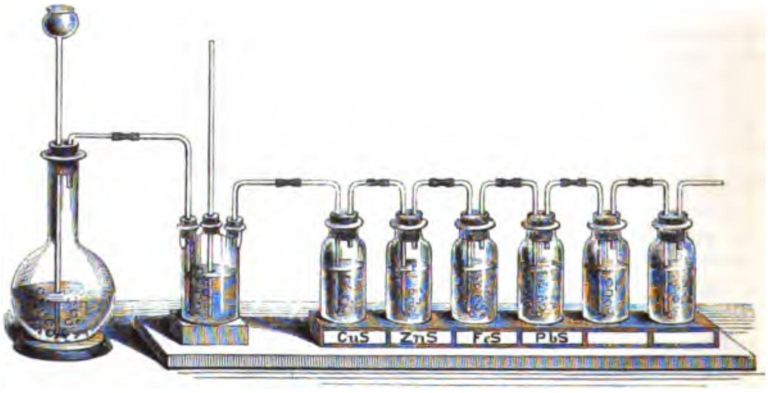

FIG. 38.

	Result.
1. Blue vitriol (or cupric sulphate)	a black precipitate.
2. White vitriol (or zincic sulphate)	a white precipitate.
3. Green vitriol (or ferrous sulphate)	a black precipitate.
4. Sugar of lead (or plumbic acetate)	a black precipitate.
5. Alum	no precipitate.
6. Epsom salt	no precipitate.

The sulphur of the sulphuretted hydrogen combines instantaneously with the metal and forms a metallic sulphide—(1) Cupric sulphide, CuS; (2) Zincic sulphide, ZnS; (3) Ferrous sulphide, FeS; (4) Plumbic sulphide, PbS, whilst the metals aluminium in alum, and magnesium in Epsom salts do not possess sufficient affinity for sulphur to form a sulphide in the wet way.

Most metallic sulphides (the alkaline sulphides excepted) are either insoluble or with difficulty soluble in water; and it is obvious, therefore, why a precipitate appeared, as soon as the sulphur of the sulphuretted hydrogen combined with the metals copper, zinc, iron, or lead.

Solution, precipitation.—We have just seen that bodies may be dissolved in water, forming what is termed a *simple solution.* The liquid in which the solution is effected is termed a *solvent.* Water (distilled) is most frequently employed for this purpose; other solvents, *e.g.*, alcohol, ether, chloroform, etc., are occasionally but rarely employed. A finely-divided substance dissolves more readily than a coarse powder or a crystalline body; it also, with very few exceptions, dissolves more rapidly and to a greater extent in hot than in cold water.

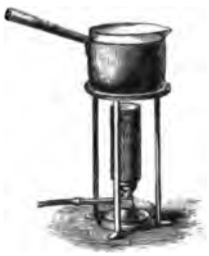

FIG. 39.

A solid body can be recovered from its solution by *evaporation.* This may be effected by heating the solution in a porcelain dish over a water-bath (Fig. 39) or over the bare flame, by so regulating the heat as to prevent loss by spurting; or it may be recovered by modifying or removing *the solvent;* NaCl, *e.g.*, which is soluble in water, is precipitated on the addition of concentrated hydrochloric acid; calcic carbonate dissolved in carbonic acid by the removal of the gaseous solvent on boiling; or, lastly, by the *sudden conversion of the liquid into a solid body* by the action of another body, induced by greater chemical affinity, one substance remaining in solution as a general rule.

The body which is precipitated is termed the *precipitate.* It generally sinks to the bottom of the glass vessel (test-tube, etc.) on account of its greater specific gravity. Stirring, as well as the application of heat, frequently promotes the subsidence of the precipitate. We speak of *pulverulent* (or amorphous), *crystalline*, *flaky*, *curdy*, *gelatinous* precipitates, according to the appearance which they present. This and the colour of a precipitate assists materially in identifying a body.

The body which precipitates another body is called the *precipitant.*

QUESTIONS AND EXERCISES.

1. How does sulphur occur in nature?
2. What are the properties of sulphur—1st, at the ordinary temperature; 2nd, when heated to 111° C.; 3rd, at a temperature of 250–260° C.?
3. Define a metallic sulphide.
4. Explain what changes take place when sulphur is heated, 1° out of contact with the air, and 2° with free access of air.
5. In what proportions by weight does sulphur combine on ignition with oxygen, and what will be the volume weight and the molecular weight of the product of combustion?
6. How would you explain the fact that no contraction of volume takes place

when sulphur and oxygen combine, and how does a knowledge of the density of oxygen and sulphurous anhydride, as compared with air, enable you to prove the volume composition of SO_2?

7. Explain the terms *roll sulphur* or *brimstone*, *flowers of sulphur*, *distilled sulphur*, *copper pyrites*, *galena*, *iron pyrites*.
8. How is cinnabar prepared?
9. Describe the preparation of sulphuretted hydrogen from ferrous sulphide, and state briefly its properties: give equations.
10. What are the products of the combustion of sulphuretted hydrogen in air? Express the changes by equations?
11. What change does a solution of sulphuretted hydrogen in water undergo when exposed to air?
12. How would you extract sulphur from iron pyrites?
13. Calculate the percentage composition of SH_2.
14. State whether the atomic weights of SH_2 and SO_2 are identical with the molecular weights.
15. What is the density of SO_2 and SH_2 compared with hydrogen, and what is the weight in grms. of one litre of the respective gases?
16. How would you demonstrate experimentally the action of SH_2 upon different saline solutions, such as a solution of sugar of lead, blue and green vitriol, etc.?
17. You have given to you iron filings, flowers of sulphur, and dilute hydrochloric acid: describe accurately the different chemical changes which, in your opinion, can be produced with these materials.
18. State how you would purify a sample of *rough sulphur* containing from three to four per cent. of earthy impurities.

CHAPTER VIII.

CHLORINE, its Properties.—CHLORIDES.

Experiment 44.—When a well known mineral called *black oxide of manganese*, MnO_2, composed of one atom of the metal manganese and two atoms of oxygen, is gently heated with concentrated hydrochloric acid in a generating flask (Fig. 40), a yellowish green gas, called *chlorine*,* is evolved, which cannot, even when largely diluted with air, be inhaled without danger, on account of its

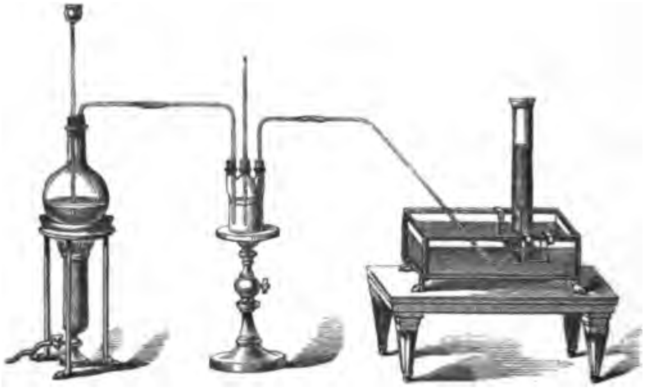

FIG. 40.—PREPARATION OF CHLORINE GAS.

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* From χλωρός, yellowish green.

highly poisonous nature, and the black oxide of manganese dissolves to a yellowish coloured liquid, containing manganous chloride, $MnCl_2$. The reaction takes place in two stages—

$$1.\ MnO_2 + 4HCl = MnCl_4 + 2OH_2$$
$$2.\ MnCl_4 = MnCl_2 + Cl_2.$$

Chlorine gas, like hydric sulphide, is soluble in water, and a solution of chlorine may be obtained by passing the gas for some time into cold water. The gas can be collected over warm water in a pneumatic trough, as seen in Fig. 41, or it may also be collected by displacement, *i.e.*, the delivery-tube is passed to the bottom of an upright glass cylinder, or test tube, till the whole of the cylinder is filled with the yellowish green gas. The lighter air is gradually lifted out of the cylinder by the heavier chlorine. The operation of collecting a highly poisonous gas like chlorine must be carried on in a well ventilated closet. Cylinder after cylinder may thus be filled with chlorine. Absolute displacement of the air is not possible, nor is it of much consequence. The edge of the cylinder is slightly greased, and a glass plate, when gently pressed down upon the opening, effectually shuts in the gas.

Chlorine gas is considerably heavier than air, its specific gravity, compared with air, is 2·46, or $\frac{2{\cdot}46}{{\cdot}0693} = 35{\cdot}5$, when compared with hydrogen gas.

1 litre of chlorine gas therefore weighs 35·5 criths, or 35·5 × ·0896 grm., = 3·1808 grm. It is a two volume gas $\boxed{Cl \,\vdots\, Cl}$, and its molecular weight is 2 × 35·5 = 71.

Experiment 45.—Introduce into a cylinder charged with chlorine gas, flowers of various colours, a strip of litmus-paper, a piece of moistened cotton print, printed and written slips of paper, and cover over with the glass plate. The colours of the flowers disappear; violets, ex. gr., become quite colourless; the cotton print is turned white; the ink acquires a reddish-brown appearance; the printing ink alone, or the finely divided carbon which it contains (lamp-black) remains unaffected.

This proves, then, that chlorine is a *powerful bleaching agent.* Hence its application in the arts and manufactures. Linen and cotton goods are bleached by the agency of chlorine, and paper pulp is rendered white. Silk or woollen stuffs, however, cannot be bleached by chlorine, because the fibres of these fabrics are destroyed by it. Chlorine water bleaches equally well.

A *solution* of chlorine in water is a useful reagent in the laboratory.

Experiment 46.—The solution is prepared by passing a current of chlorine gas through Woulfe's bottles, as seen in Fig. 41. The contents of the Woulfe's bottle nearest to the generating flask are generally contaminated with some hydrochloric acid, which has been carried over by the chlorine, and are best rejected. A simpler method of making a saturated solution of chlorine consists in passing the gas from the first Woulfe's bottle to a retort inverted, as seen in Fig. 42, containing cold distilled water.

A solution of chlorine in water has the same yellowish green colour as the gas itself. It becomes gradually decomposed when exposed to sunlight, especially to direct sunlight, as the hydrogen of the water goes to the chlorine to form hydrochloric acid (HCl), and the oxygen is liberated—

$$OH_2 + Cl_2 = 2HCl + O.$$

The bleaching action of chlorine depends upon the same chemical change; it is an indirect process of *oxidation*.

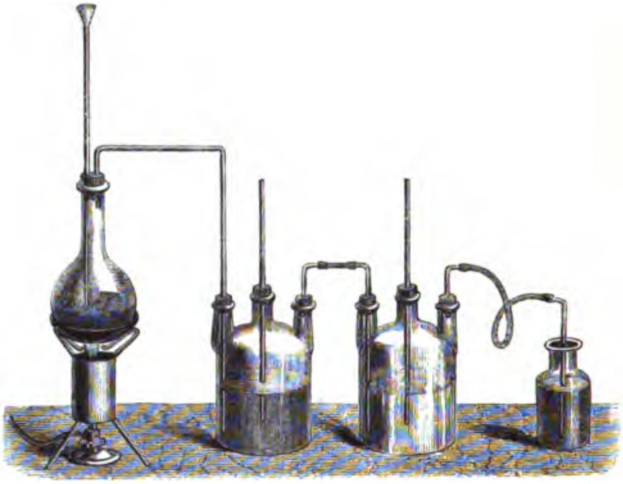

FIG. 41.—PREPARATION OF CHLORINE WATER.

Experiment 47.—Place a burning taper in a cylinder and hold a second cylinder filled with chlorine gas to the mouth of the upright cylinder, as seen in Fig. 43. The candle continues to burn with a feeble yellowish flame, and heavy clouds of smoke or soot are seen to separate.

FIG. 42.

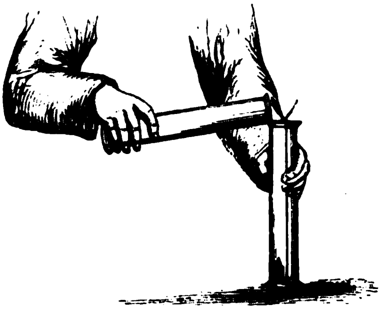

FIG. 43.

A candle, whether made of paraffin, wax, tallow or spermaceti, consists of carbon and hydrogen, or of carbon, hydrogen and oxygen, in varying proportions. The chlorine acting upon the hydrogen sets the carbon free in the form of solid particles or black soot. This then proves that the white material of which candles are made, contains carbon, and that chlorine has a stronger affinity for hydrogen than for carbon. The chlorine forms with the hydrogen a binary compound—an acid—known as hydrochloric acid or hydric chloride. This can be shown by rinsing out the cylinder with a little water and testing with blue litmus paper.

Experiment 48.—Powder some metallic antimony very finely and place the powder in a fine sieve sufficiently large to cover the opening of a tall glass cylinder filled with chlorine gas. Shake the sieve gently. Some of the finely divided antimony falls through into the chlorine gas and combines with it, giving rise to quite a rain of fire, and the cylinder becomes filled with thick white fumes. The chlorine gas combines directly with the metal antimony—

$$Sb + Cl_3 = Sb\,Cl_3,$$

and the chemical change is accompanied by great heat, and the phenomenon of light.

A similar but less energetic action is observed when chlorine is made to act in a retort or tube of hard glass, upon metallic copper or zinc; only the reaction has to be started and assisted by the application of heat. Flashes of light are likewise given out during the combination of the metals with the gas chlorine. The compounds so formed were found on analysis to be composed of 1 atom of the metal to 2 atoms of the gas chlorine, *e.g.*, $CuCl_2$ $ZnCl_2$.

Experiment 49.—Set fire to some magnesium wire and introduce the burning magnesium quickly into a cylinder filled with chlorine gas. It continues to burn with great brilliancy in the gas. The product of the combustion of magnesium in chlorine is a white powder, magnesic chloride ($MgCl_2$), which on exposure to the air rapidly attracts moisture and liquefies. Test the liquid. It is neutral to test-papers.

Experiment 50.—Fill a good sized stoppered bottle (Fig. 44) with dry chlorine gas, then introduce a few pieces of sodium cut into thin slices, and close the bottle with a good cork and allow to stand for some time. The bright metal is seen to become coated over after a few minutes with a white film which grows thicker till it peels off at last. The yellowish green gas disappears after about 24 hours, when the greater part of the metal has become converted into a white powder. The cork is removed with difficulty; because by the absorption of the gas by the metal sodium, a vacuum has been created in the bottle, and the air rushes in with considerable violence, as soon as the cork is removed. Take out the white powder. Detach any metal that has not been acted upon, and dissolve the powder in a little water.

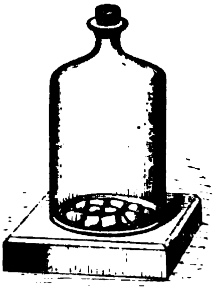

FIG. 44.—COMBINAIOTN OF CHLORINE AND SODIUM.

The solution shows no action upon either blue or red litmus-paper; it is an indifferent or neutral liquid; it tastes neither sour (acid) nor caustic (alkaline). It has the taste of common salt. In fact, *by the combination of the metal sodium and the gas chlorine, we have produced common salt*, and have proved thereby that our common table salt—*sodic chloride* (NaCl)—consists of two elementary bodies, of sodium and of chlorine.

Nature of Metallic Chlorides.—As all metallic chlorides, with the exception of the chlorides of platinum and gold, can be prepared like sodic chloride by the direct combination of a metal and chlorine, they must be analogous to this well known salt, and the latter may be regarded as the representative of metallic chlorides generally. From the most remote times sodic chloride has received the name of *salt*, and has always been known as " the salt." The same name in its generic construction is now assigned to other metallic chlorides. They are distinguished from the corresponding metallic oxides by their reaction on vegetable colours (litmus papers). Not one metallic chloride possesses an alkaline reaction, the chlorides of some of the heavy metals giving even an acid reaction; whilst the corresponding oxides have either a strongly alkaline (caustic) character, or show no reaction at all with litmus.

Sodic chloride is found in nature very widely distributed. From one of its sources, viz., sea-water, it is obtained by *evaporation* and *crystallisation*. The so-called *mother liquor* (or concentrated saline solution from which salt has been removed by crystallisation) has been found to contain two other elementary bodies, bromine and iodine which closely resemble chlorine in their properties. They exist chiefly in combination with magnesium, as bromide and iodide of magnesium. These elements can likewise be isolated. *Bromine** (symbol Br.), at the ordinary temperature, is a dark brownish disagreeably smelling, very poisonous liquid. *Iodine*† (symbol I) is a crystalline substance of dark steel or deep violet colour, subliming in beautiful violet vapour, when a small crystal of it is gently heated in a test-tube. These two elements, together with another elementary body, found in fluor spar, called *fluorine* (symbol F), (never isolated as yet), can likewise combine with metals, and are classed together with chlorine under the name of *halogens* or *salt formers* (from ἅλς, salt, and γεννάω, I generate). They also combine with hydrogen and form acids—gaseous like hydrochloric acid gas, and eagerly absorbed by water. These acids are called—

Hydrobromic acid (Hydric bromide) HBr.
Hydriodic „ („ iodide) HI.
Hydrofluoric „ („ fluoride) HF.

Their consideration will be reserved for the second part or the study of *qualitative* analysis.

Chlorine combines with non-metals (metalloids) as well as with metals. Chemical combination takes place between them with great energy, mostly marked by flashes of light and evolution of much heat. Phosphorus, sulphur, and carbon form chlorides, although the latter element cannot combine directly with chlorine. A knowledge of these compounds is, however, best acquired by attending a course of lectures, since the explanation of the chemical changes involved in their formation would, to a great extent, be mere repetition of what has already been studied. The most important compound is that which chlorine forms with hydrogen.

Experiment 51.—A wide capacious flask (Fig. 45) is filled by upward displacement with chlorine gas. A gas-holder filled with hydrogen furnishes a steady supply of gas. A glass tube bent in the manner shown by the figure is drawn out to a jet, and connected with the delivery-tube by means of india-rubber tubing; the gas is lit, and the burning jet rapidly introduced into the flask. It continues to burn for some time with a bright blue flame. The flame dies gradually away; and on removing the delivery-tube and closing the mouth of the flask rapidly with the flat of the hand or a cork, and introducing it, mouth downward, into cold water, and then withdrawing the hand or the cork, the water rushes into the flask and nearly fills it. Remove the flask by inserting the cork and test its contents with litmus-paper. The liquid reddens blue litmus-paper instantaneously. It contains an *acid gas* which is *eagerly absorbed by water*. From its origin, it can only be hydrochloric acid gas or hydric chloride, and the liquid a very dilute hydrochloric acid solution.

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* From βρῶμος, a stench.

† From ἰώδης, violet-coloured.

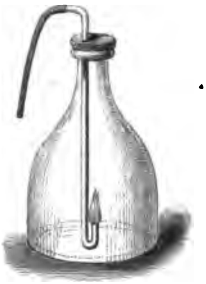


FIG. 45.—COMBUSTION OF HYDROGEN IN CHLORINE.

Properties of the gas.—Hydrochloric acid forms a colourless gas of pungent acid odour. Its combining proportions by volume may be represented as follows:—

$$\boxed{\mathrm{H} \quad \mathrm{H}} + \boxed{\mathrm{Cl} \quad \mathrm{Cl}} = 2\ \boxed{\mathrm{H} \quad \mathrm{Cl}}$$

i.e., 1 molecular volume of chlorine gas on combining with a molecular volume of hydrogen, forms two molecular volumes of hydrochloric acid gas. The two gases combine without contracting. Combination takes place with explosive violence when a mixture of hydrogen and chlorine is exposed to *direct sunlight*, slowly only when left exposed to *diffused daylight*, and not at all at the ordinary temperature when placed in darkness. The specific gravity of hydrochloric acid gas compared with air is 1·262 and compared with hydrogen $\frac{1{\cdot}262}{{\cdot}0693} = 18{\cdot}25$, *i.e.*, 1 litre of hydrochloric acid weighs $\frac{1 + 35{\cdot}5}{2} = \frac{36{\cdot}5}{2} = 18{\cdot}25$ times as much as 1 litre of hydrogen or 18·25 criths, equal to 18·25 × ·0896 grm. or 1·6352 grm. The molecular weight of hydrochloric acid gas is 36·5. It is most eagerly absorbed by water—one litre of water is capable of absorbing 500 litres of gas at 0° C. Water so saturated fumes in the air, the vapour of the acid combining with the moisture in the air, and the liquid constitutes the ordinary commercial fuming hydrochloric acid.

Bromine, iodine and fluorine when combined with hydrogen form likewise acid liquids, which possess considerable interest, they will be considered more fully hereafter.

As these acids contain no oxygen, like the acids with which we have already become acquainted, they have been called *hydrogen* acids or simply *hydro-acids*, as distinguished from *oxygen* or *oxy-acids*. Oxygen then is not the only element which can by its combination with other elements form acids, as was thought at the time when this element was first discovered, and when it received the name oxygen or *generator of acids*. In fact, on comparing the compounds which oxygen forms with metals, such as potassium or sodium (which are perhaps only of a *basic* character, since these powerful metals neutralize and actually overpower the acidifying properties of oxygen), with the compounds which potassium and sodium form with chlorine, it is obvious, that chlorine rather deserves to be called an *acid generator*: for the compound which it forms with hydrogen is a *powerful acid*, and its compounds with potassium and sodium are neutral or indifferent bodies, the metals obviously not being capable of overpowering to the same extent the acidifying properties of chlorine as they overpower those of oxygen. This acidifying property of chlorine becomes still more apparent, when we compare some of the chlorides of the heavy metals which are strongly acid, with the corresponding oxides which are mostly quite indifferent bodies.

QUESTIONS AND EXERCISES.

1. How is chlorine prepared? Give equations.
2. Describe briefly the properties of chlorine.
3. Explain the bleaching action of chlorine.
4. State how chlorine water becomes decomposed when exposed to sunlight.
5. Define a metallic chloride. Describe instances of the direct combination of chlorine with metals.
6. Show in what respect metallic chlorides differ from metallic oxides.
7. Explain the meaning of the terms *chlorine*, *bromine*, *iodine*, and *fluorine*.
8. Enumerate briefly the distinguishing features of chlorine, bromine, and iodine.
9. Explain the terms *halogen*, *hydro-acid*, *hydric chloride*.
10. How is hydrochloric acid gas prepared, and what are its most characteristic properties?
11. What is the volume weight and the molecular weight of chlorine and of hydrochloric acid gas?
12. What is the weight of one litre of Cl and of a litre of HCl in grammes?
13. You have given to you black oxide of manganese, concentrated hydrochloric acid, and metallic antimony; state what chemical changes you can produce with these materials.
14. The density of hydrogen gas compared with air is ·0693, that of chlorine gas 2·46; find, from these figures, the atomic weight of chlorine.
15. Calculate the percentage composition of HCl and of NaCl.

Chapter IX.

APPLICATION of the THEORY of CONSTANT CHEMICAL COMBINING PROPORTIONS.

Symbolic formulæ have hitherto served—

1st. To represent bodies, elementary or compound.

2nd. To illustrate, in the briefest manner, the play of chemical affinities, the breaking up of existing chemical compounds, and the building up of new bodies.

They serve, however, another and most important purpose, for they also bear, as has been already remarked (Chapter VI), the impression of the respective atomic weights of the element or compound body which they denote.

Equations illustrating chemical changes express likewise the relative *quantities* of the elements which form the compounds acting upon each other, or which take part in the changes, and hence they furnish the basis for *quantitative* chemical calculations. Thus the formation of cupric oxide by the action of oxygen on copper is expressed by the equation—

$$\mathrm{Cu + O = CuO}$$

which conveys to the mind at the same time the idea that one atom of copper combines with one atom of oxygen to form the molecule cupric oxide (the atomic weight of copper being 63·5, that of oxygen 16); and our equation tells us, by a process of simple substitution, that 16 parts by weight of oxygen combine with 63·5 parts by weight of copper, and that the two together must form 79·5 parts by weight of cupric oxide. The symbolic equation is thus transcribed arithmetically—

$$63{\cdot}5 + 16 = 79{\cdot}5$$

and it is easy to calculate the quantities of copper and oxygen involved in the formation of a given quantity of cupric oxide, and the quantity of cupric oxide obtained from known quantities of copper and oxygen.

Questions such as the following will now readily be answered by a mere calculation of rule of three:

1. How much Cu combines with a given quantity of O?
2. „ O „ „ Cu?
3. „ CuO can be formed from „ Cu?
4. „ Cu is contained in a „ CuO?
5. „ O „ „ CuO?

If we wish to know—1st, how much cupric oxide, CuO, we can get by the oxidation of 100 grains of copper, we have—

$$63{\cdot}5 \;:\; 79{\cdot}5 \;::\; 100 \;:\; x.$$

Atomic weight of copper. **Atomic weight of cupric oxide.**

Ans. = 125·19 *grs. of CuO.*

2. How much copper is left when 100 grains of cupric oxide, CuO, are reduced in a current of hydrogen gas?

$$79{\cdot}5 \;:\; 63{\cdot}5 \;::\; 100 \;:\; x.$$

Atomic weight of cupric oxide. **Atomic weight of copper.**

Ans. = 79·87 *grs. of Cu.*

3. How much mercury, Hg, is required to form 20 grms. of mercuric oxide, HgO?

$$216 : 200 :: 20 : x.$$

216	200
Atomic weight of HgO.	Atomic weight of Hg.

Ans. 18·51 *grms.*

4. How much iron, Fe, has to be taken to produce 100 lbs. of ferrous sulphide, FeS?

$$88 : 56 :: 100 : x.$$

88	56
Atomic weight of FeS.	Atomic weight of Fe.

Ans. 63·63 *lbs.*

5. How much ferrous sulphide can be obtained by the combination of iron with 50 lbs. of sulphur?

$$32 : 88 :: 50 : x.$$

32	88
Atomic weight of S.	Atomic weight of FeS.

Ans. 137·5 *lbs.*

6. How much hydrogen by weight, and by volume (in litres), is required to reduce 25 grms. of cupric oxide, CuO, to metallic copper?

$$79{\cdot}5 : 2 :: 25 : x.$$

79·5	2
Atomic weight of CuO.	Atomic weight of two atoms of H.

Ans. ·6289 *grm. of H.*

On dividing ·6289 grm. by the weight of one litre of hydrogen, measured at 0° and 760 mm. barometrical pressure, viz., ·0896 grm., or a crith, we obtain the number of litres of hydrogen gas at the same temperature and pressure—

$$\frac{\cdot 6289}{\cdot 0896}$$ *Ans.* 7·01 *litres of H.*

7. How much sulphurous anhydride, SO_2, is obtained by the combustion of 10 grms. of sulphur in oxygen gas—1st, by weight; 2nd, by volume (litres)?

$$32 : 64 : 10 : x.$$

32	64
Atomic weight of S.	Atomic weight of SO_2.

Ans. 20 *grms. of* SO_2.

The volume weight of SO_2 is 32 criths, or 2·8672 grms. and by dividing the total weight of sulphurous anhydride obtained, viz., 20 grms. by the weight of one litre of the gas, we have—

$$\frac{20}{2·8672} = 6·975 \textit{ litres of } SO_2.$$

8. How much chlorine gas by weight, and by volume, can be obtained by the action of excess of hydrochloric acid on 16 grms. of black manganic oxide, MnO_2?

$$\underset{\substack{\text{Atomic}\\ \text{weight of}\\ MnO_2.}}{87} \; : \; \underset{\substack{\text{The weight of}\\ \text{a molecule}\\ \text{of chlorine.}}}{71} \; :: \; 16 \; : \; x.$$

Ans. 13·057 *grms. of Cl.*

Now one litre of chlorine weighs 35·5 criths, or ·0896 × 35·5 = 3·1808 grms.

$$\frac{13·057}{3·1808} = 4·104 \textit{ litres of chlorine gas.}$$

9. When carbon is burnt in oxygen gas it forms carbonic anhydride gas, CO_2. How much carbonic anhydride by weight, and by volume, can be obtained by thus burning 15 grms. of carbon?

$$\underset{\substack{\text{Atomic}\\ \text{weight of C.}}}{12} \; : \; \underset{\substack{\text{Atomic}\\ \text{weight of } CO_2.}}{44} \; :: \; 15 \; : \; x.$$

Ans. 55 *grms. of* CO_2.

One litre of carbonic anhydride gas weighs 22 criths, or ·0896 × 22 = 1·9712 grm.

$$\text{and } \frac{55}{1·9712} = 27·90 \textit{ litres of carbonic anhydride gas.}$$

10. How much hydrogen and oxygen by weight and by volume can be obtained, by electrolysis, from 10 grms. of water?

$$\underset{\substack{\text{Atomic}\\ \text{weight of } OH_2.}}{18} \; : \; \underset{\substack{\text{Weight of}\\ \text{mol. of hydrogen.}}}{2} \; :: \; 10 \; : \; x.$$

Ans. 1·111 *grms. of H.*
8·889 *grms. of O.*

One litre of H weighs ·0896 grm., hence—

$$\frac{1·111}{·0896} = 12·4 \text{ litres of hydrogen gas.}$$

One litre of oxygen weighs 16 times as much as one litre of hydrogen gas, *i.e.*, ·0896 × 16 = 1·4336 grm.

$$\frac{8{\cdot}889}{1{\cdot}4336} = 6{\cdot}200 \text{ litres of oxygen gas.}$$

11. Given five litres of chlorine gas, how much metallic sodium is required to convert the whole of the chlorine into sodic chloride?

Ans. 10·304 *grms. of Na.*

12. 15 grms. of ferrous sulphide are treated with dilute hydrochloric acid: how much SH_2 by weight, and by volume, can be obtained theoretically therefrom?

Ans. 5·795 *grms. by weight, and* 3·804 *litres of* SH_2.

Chapter X.

ATOMICITY OR QUANTIVALENCE OF ATOMS.

According to the law of multiple proportions, atoms can combine with atoms in more than one proportion, *i.e.*, one atom with two, three, four, or more other atoms.

Some few metals and metalloids can form only one oxide, sulphide, chloride; others two or more. Thus we have seen that binary compounds, such as:—

FeO.	FeS.	$FeCl_2$.
MgO.	MgS.	$MgCl_2$.
CuO.	CuS.	$CuCl_2$.
ZnO.	ZnS.	$ZnCl_2$.

are comparatively simple bodies. In fact, the number of atoms in the higher binary compounds of mineral or inorganic origin can mostly be expressed by the multiples 3, 4, 5.

We have seen (Experiment 46) that under the continued influence of sunlight, chlorine water is decomposed into hydrochloric acid, which is absorbed by the water, and oxygen; and that for every two volumes of chlorine gas, when placed over water, one volume of oxygen will be found after some time. Two atoms of chlorine exert therefore the same combining power as one atom of oxygen.

Experiment 2 has demonstrated that the action of dilute hydrochloric acid on zinc liberated hydrogen, whilst the chlorine remained combined with the metal zinc, forming zincic chloride. We have since seen that hydrogen and chlorine in hydrochloric acid gas are combined in equal volumes:—

$$\boxed{\mathrm{H}} + \boxed{\mathrm{Cl}} = \boxed{\mathrm{H}\ \mathrm{Cl}}$$

consequently we know that for every molecule $\boxed{\mathrm{H}\ \mathrm{H}}$ of the liberated hydrogen gas two volumes (two atoms) of chlorine remain in combination with the metal zinc, and that therefore two molecules of hydrochloric acid must have taken part in the reaction—

$$Zn + 2HCl = ZnCl_2 + H_2.$$

Zincic chloride has the composition $ZnCl_2$; one atom of zinc accordingly possesses the chemical combining power of two atoms of hydrogen, and two atoms of chlorine are of the same chemical *combining value* as one atom of oxygen (comp. Exp. 12); they are in fact *equivalentic*. The same holds good for other metals, such as calcium, iron, manganese, copper, mercury, *i.e.*, they all unite with the same number of atoms of chlorine, viz., two.

Experiment 1 has shown that the metal sodium decomposes water by taking the place of the hydrogen therein. Chlorine in Experiment 50 also combined directly with the metal forming common salt, NaCl, a compound which is in every respect analogous in constitution to hydrochloric acid, HCl. Sodic chloride can be readily prepared by the decomposition of this acid by means of sodium, hydrogen being evolved.

Experiment 52.—Heat a little concentrated hydrochloric acid in a flask (Fig. 46); it evolves abundance of hydrochloric acid gas, which must be dried by passing it through a Woulfe's bottle containing lumps of pumice-stone soaked in concentrated sulphuric acid. Collect the dry gas in a narrow cylinder over mercury, as seen in Fig. 46, and mark the level of the mercury column by means of a small india-rubber ring. If a pellet of sodium (or a lump of sodium-amalgam) be now passed up into the gas and the tube be gently agitated, the gas volume will be seen to diminish, and after a time will have contracted to one-half. On examining the remaining gas, it is found to have all the properties of hydrogen.

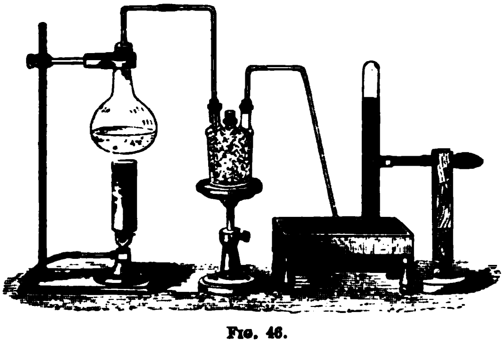


Fig. 46.

This proves that two volumes of dry hydrochloric acid gas (or a molecular volume) contain equal volumes of hydrogen and chlorine. The metal sodium combined with the chlorine, leaving the hydrogen in the free state.

One atom of sodium possesses then the same chemical displacing power as one atom of hydrogen, and two atoms of sodium must be required to combine with one atom of oxygen (in the same manner as two atoms of hydrogen were required to combine with one atom of oxygen in water), and the formula of the resulting sodic oxide must therefore be written—

$$Na_2O.$$

The same holds good for several other metals, viz., potassium, silver; and the respective formulæ of the chlorides, and oxides of these metals are therefore—

$NaCl.$	$Na_2O.$
$KCl.$	$K_2O.$
$AgCl.$	$Ag_2O.$

Other metals again combine with 3, 4, 5, or 6 atoms of chlorine, or 1½, 2, 2½, and 3 of oxygen; such as the metals gold, tin, antimony, chromium. Their respective oxides and chlorides are thus written—

*$AuCl_3.$	$Au_2O_3.$
$SnCl_4.$	$SnO_2.$
$SbCl_5.$	$Sb_2O_5.$
	$CrO_3.$

$AuO_{1\frac{1}{2}}$ and $SbO_{2\frac{1}{2}}$ being inadmissible for reasons already stated.

Sulphur forms with metals compounds almost precisely analogous to those which oxygen forms.

In order to mark the binding capacity or atom-fixing power (called *atomicity* or *quantivalence*) of the various metals, six divisions have been adopted by chemists, of which the following metals may be regarded as the representatives:—

Na, Mg, Au, Sn, Sb, Cr.

A metal which combines with 1 atom of chlorine is *monovalentic* or *monadic;* other metals which combine with 2, 3, 4, and 5 atoms of chlorine (or in the place of 6 of chlorine with 3 of oxygen), are *di-*, *tri-*, *tetra-*, *penta-*, and *hexa-valentic* (from *valere*—to be of value), shortly called *monads*, *dyads*, *triads*, *tetrads*, *pentads*, and *hexads.* Elements with an odd number of bonds are called by Dr. Odling *perissads* (from περισσός, uneven, odd); whilst those with an even number are termed *artiads* (from ἄρτιος, even).

---

* When the molecule of a compound contains more than one atom or combining proportion of an element, a coefficient is placed *after* the symbol of the element.

Oxygen, we have seen, is combined in water with two atoms of hydrogen: it is therefore divalentic, or one atom of oxygen is equivalent to two atoms of hydrogen. Sulphur in sulphuretted hydrogen is divalentic; and one atom of sulphur is equivalent to two atoms of hydrogen.

Boron combines with three atoms of chlorine to form boric chloride, BCl_3. Carbon combines with four atoms of hydrogen to form marsh-gas, CH_4, one of the constituents of coal gas. Pentavalentic elements are the elements constituting the nitrogen group, N,P,As, and Sb.

Hydrogen is thus called upon to perform fresh functions, for it forms also *the unit of the binding or atom-fixing as well as atom-displacing power* inherent in every elementary body, as it already constituted the unit of atomic and volume combination. This atom-fixing power of elements is well illustrated whenever elements combine directly with hydrogen; as when oxygen attracts to itself two, nitrogen three, or carbon four, atoms of hydrogen.

It must not be supposed that in the absence of metallic compounds with hydrogen, the combining capacity of metals (and non-metals) for chlorine—the equivalent for hydrogen—has been the only criterion for determining the atomicity or quantivalence of the different elements. Comparatively modern discoveries in the chemistry of organic bodies, in which metals are combined with a certain number of atoms of the organic analogues of hydrogen, methyl, ethyl, etc., have but recently introduced this method of determination. The coefficients of atomicity are, moreover, not yet determined experimentally for all metals, and we have in many cases to assume them by reasoning from analogy only. But whilst the atomicity of many elements must still be considered as provisional, and open to revision, yet the system of classification founded upon atom-fixing power has so much simplified the study of chemistry, that its introduction, even in its present incomplete state, into text books, cannot fail to recommend itself strongly to the student, as it supplies him with a generalisation which greatly facilitates the comprehension of chemical phenomena. Moreover, the doctrine of atomicity is in strict harmony with the atomic hypothesis.

We connect, then, with atoms not merely the notion of indivisibility and a definite relative atom- and volume-weight, but likewise varying degrees of inherent affinity and a capacity of fixing or displacing a definite number of other atoms. Thus the atomic theory gains in importance as it gains in extent.

Symbolic representation of the powers of Atoms in fixing or displacing other Atoms.

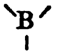
We represent to ourselves atoms as the smallest possible particles of matter, and in the absence of any experimental evidence as to their form may, for the sake of convenience, view them as spheres. We explain chemical combination between two elements as arising from the intimate union which takes place between their atoms, owing to the chemical affinity peculiar to each individual atom. If an atom exhibits an affinity by which its atom-fixing power becomes exhausted by combining with an atom of another element whose atom-fixing power equals that of hydrogen, taken as unit, it is manifestly a *monovalentic* element or a monad,—it can bind or satisfy only one affinity. The atomicity of an element such as hydrogen or chlorine may be represented graphically, thus:—

Monad Atom H– Molecule H–H.
„ Cl– „ Cl–Cl.

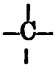
An atom of an element like magnesium, capable of fixing two monad atoms of chlorine, would then have to be represented graphically, thus:—

Dyad Atom –Mg–

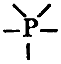
An element capable of fixing 3 atoms of chlorine, thus:—

Triad Atom 

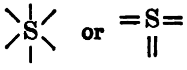
An element capable of fixing 4 atoms of hydrogen, thus:—

Tetrad Atom 

An element capable of fixing 5 atoms of chlorine, thus:—

Pentad Atom 

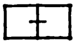
An element capable of fixing 3 atoms of the dyad oxygen, thus:—

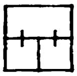
Hexad Atom 

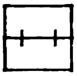
Symbolic notation conveys the same idea if we employ dashes, and for the higher atomicities Roman figures placed to the right-hand side slightly above the symbols, thus:—

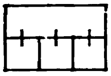
Hydrogen....	H' (written mostly without the dash).
Oxygen......	O''
Boron	B'''
Carbon	C^{iv}
Phosphorus ..	P^{v}
Sulphur......	S^{vi}

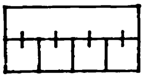
Other modes of graphic representation would answer equally well and have actually been used for this purpose, thus:—

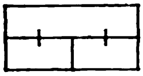
 = molecule HH, or ClCl, HCl, NaCl, AgCl.


= molecule OH_2, or SH_2, OAg_2, OK_2.


= molecule CuO, or HgO.


= molecule $AuCl_3$.


= molecule CH_4, or $SnCl_4$.


= molecule SO_2, or CO_2.

This method of graphic representation possesses the advantage of setting forth in a marked manner the quantivalence of atoms as well as their molecular combining conditions. The second formula, *e.g.*, shows at a glance that two atoms of hydrogen are combined with one atom of oxygen, and that, therefore, the atom oxygen is equivalentic to two atoms of hydrogen. Formula 5 shows in like manner that four atoms of hydrogen are combined with one atom of carbon, and hence that this latter element is equivalentic to four atoms of hydrogen or chlorine.

At the same time this graphic representation is liable to mislead if the idea be entertained for a moment that an atom of carbon is four times, or an atom of oxygen twice as large as an atom of hydrogen or chlorine; and as no graphic representation whatever can claim to elucidate "*either the shape or size of an atom or molecule, nor the relative position of the constituent atoms of any chemical compound*," it will suffice if we simply link together their symbols by short connecting lines, in order to indicate their atom-fixing capacity.

Thus we write:—

$$\mathrm{Cl—Cl}$$

$$\mathrm{H—O—H}$$

In the following table, taken from Dr. Frankland's "Lecture Notes," page 32, will be found the 36 most important elements, classified according to their atomicity or respective quantivalence. Metalloids are printed in *italics*. The different classes are again subdivided into sections, representing elements closely resembling each other in their chemical character:—

Monads, or Monovalentic Elements.	**Dyads, or Divalentic Elements.**	**Triads, or Trivalentic Elements.**	**Tetrads, or Tetravalentic Elements.**	**Pentads, or Pentavalentic Elements.**	**Hexads, or Hexavalentic Elements.**
1st Section.	*1st Section.*	*1st Section.*	*1st Section.*	*1st Section.*	*1st Section.*
Hydrogen.	*Oxygen.*	*Boron.*	*Carbon.* *Silicon.* Tin.	*Nitrogen.* *Phosphorus.* Arsenic. Antimony. Bismuth.	*Sulphur.*
2nd Section.	*2nd Section.*	*2nd Section.*	*2nd Section.*		*2nd Section.*
Fluorine. *Chlorine.* *Bromine.* *Iodine.*	Barium. Strontium. Calcium. Magnesium. Zinc.	Gold.	Aluminium.		Chromium. Manganese. Iron. Cobalt. Nickel.
3rd Section.	*3rd Section.*		*3rd Section.*		
Potassium. Sodium.	Cadmium. Mercury. Copper.		Platinum.		
4th Section.			*4th Section.*		
Silver.			Lead.		

The elements have been classified according to their highest *atomicity* or greatest number of bonds. Thus sulphur *can* be made to combine with 3 atoms of the dyad element oxygen, although under ordinary conditions it combines only with 2 atoms of oxygen to form sulphurous anhydride gas, SO_2. In this instance the sulphur acts the part of a tetrad. Again, sulphur combines with two atoms of hydrogen, and is then for the time being a dyad element. The active atomicity or quantivalence of an element therefore principally depends on the nature of the elements with which it enters into combination. A hexad atom does not necessarily combine always with its maximum number of 6 chlorine atoms, or 3 atoms of oxygen, &c.: it may bind only 4 atoms of chlorine or 2 atoms of a dyad element, such as oxygen or sulphur; or 2 atoms of chlorine or its equivalent of a dyad atom: but a hexad atom will never be found to link itself to 5 or 3 or 1 atom of a monad element. *Its atomicity co-efficient is invariably an even number.* If the co-efficient be 2 or 4, instead of 6,—4 or 2 bonds respectively become, so to speak, *dormant* or *inactive;* but the *absolute* atom-fixing power of the hexad remains the same, and the dormant, or *latent* bonds, as Dr. Frankland calls them, may be called into activity by fresh chemical agencies, whenever it is desired. The sum of the active and latent bonds must evidently always be equal to the absolute atomicity of an element.

Then, again, a pentad atom need not necessarily combine with 5 atoms of chlorine, &c. It may exist in combination with 3 atoms, or 1 atom, but never with 4 or 2 atoms of chlorine, or its equivalent. *Its atomicity co-efficient is invariably an uneven number.*

Elements which in the above list are classified as *monads*, &c.,

may possibly be discovered to be capable of a higher binding power. Compounds may exist, or may yet be discovered, in which the monad element exists as a triad or pentad, or the tetrad or hexad element as a hexad or octad; but it may safely be predicted that a monad element will never bind 2 atoms of chlorine, but only 3 or 5, and that its atomicity co-efficient will be found to be an uneven number, and that of a dyad always an even one.

Use of Thick Type.—The formulæ of the different chemical compounds are, according to Dr. Frankland's system, written in such a manner as to denote "that the element represented by the first "symbol of a formula, is directly united with all the active bonds of "the other elements or compound radicals following upon the same "line." Thus the formula of water, $\mathbf{O}H_2$, signifies that the dyad atom of oxygen is combined with the two bonds of the two atoms of hydrogen. The formula of carbonic anhydride, $\mathbf{C}O_2$, signifies that the tetrad atom of carbon is combined with the four bonds of the two atoms of dyad oxygen. The first symbol constitutes the *grouping* element, and whenever this element has more than one bond, it will always be printed in thick type. The element having the greatest number of bonds will, as a rule, occupy this prominent position.

QUESTIONS AND EXERCISES.

1. Explain the action of sunlight upon chlorine water. Express the change which takes place by an equation.
2. Give reasons why two molecules of hydrochloric acid (HCl) are required to act upon an atom of zinc.
3. How would you demonstrate experimentally that hydrochloric acid gas is composed of equal volumes of H and Cl?
4. Explain why you consider that two atoms of H are equivalentic to one atom of O or one atom of Zn.
5. Assign reasons for the formulæ Na Cl and $\mathbf{O}Na_2$.
6. Classify the following elements according to their respective atom-fixing power:—Br, B, C, N, Sn, S. Mg, Ag, Cd, Pt, Si, As, Mn.
7. Commit to memory the 36 most important elements as classified in the preceding table.
8. Explain the terms *perissads* and *artiads*.
9. How can the atomicity of elements be indicated, 1st symbolically, 2nd graphically?
10. Explain what you understand by *absolute atomicity*, *active* and *latent bonds*, *grouping elements*.
11. Describe the use of thick type.
12. State how many atoms of the following elements Cl, O, S, you consider equivalent to an atom of copper, of silver, or of antimony.
13. Represent graphically a molecular volume of HCl, $\mathbf{O}H_2$, $\mathbf{B}Cl_3$, $\mathbf{C}H_4$, so as to indicate the atomicity of the respective elements, and state what objections can be urged against such graphic representation.
14. Place the atomicity co-efficient against the following elements:—P, Hg, Sr, F, I, Cr, Au.

CHAPTER XI.

HYDRATES.—REACTIONS IN THE WET WAY.

IN most of the reactions hitherto described we have restricted ourselves to changes which take place in the *dry* way, between solid bodies. In the few instances in which a liquid body reacted upon a solid body—as in the case where metallic sulphides were formed by the combination of a metal with the liquid sulphur, or where a liquid metal, such as mercury, or a readily fusible metal, like sodium, combined with oxygen or chlorine—one of the reacting bodies was rendered liquid by the application of heat. Such changes are called *reactions in the dry way*.

There are, however, a vast number of reactions, where the presence of water forms an essential feature, either by virtue of its solvent action (whereby substances are brought into more intimate contact), or by giving up a part or the whole of its constituent elements for the formation of the molecules of the new body. Such changes are termed *reactions in the wet way*.

Certain bodies, as soda, eagerly attract to themselves the moisture contained in our atmosphere. There can be no doubt that a *chemical* combination takes place between these bodies and the water, accompanied by the liberation of much heat. This is proved moreover, by the difficulty with which soda gives up its water again when heated.

Experiment 53.—Evaporate a little caustic soda in a small iron basin, or, better still, in a silver crucible or evaporating dish. It loses water, and acquires a syrupy consistency. On cooling, the mass solidifies.

Quantitative experiments have shown that one molecule of water is retained by the fused mass for every molecule of soda, $\mathbf{O}Na_2$. Dry soda, such as is formed by the oxidation of the metal sodium in a current of dry oxygen gas, combines with 1 molecule of water, and the change may be viewed as an addition of two binary compounds according to the equation—

$\mathbf{O}Na_2 + \mathbf{O}H_2 = Na_2H_2O_2$, or $2\mathbf{O}HNa$.*

The new *ternary* body contains the elements of soda and water truly chemically combined. In fact, soda acquires its characteristic caustic nature only by this very act of combination with water—$\mathbf{O}Na_2$ is without action upon dry litmus paper.

Experiment 54.—A little burnt lime, $\mathbf{Ca}O$ (quicklime), is placed in a porcelain dish, and moistened with as much water as it will take up within its pores. The mass soon begins to get hot; it gives off steam, and falls to pieces.

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* A figure placed on the left of a *group* of elements multiplies each element.

Much heat is evolved by the chemical combination of lime with water. Quantitative experiments have proved that this reaction takes place according to the equation—

$$CaO + OH_2 = CaH_2O_2.$$

Experiment has shown that phosphoric anhydride, P_2O_5, absorbs moisture with great avidity from the atmosphere. A few flakes of the anhydride when thrown into water, cause a hissing noise, and dissolve instantaneously, giving rise to an increase of temperature.

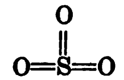
Sulphuric anhydride, SO_3, is obtained as a white mass of crystals, resembling asbestos. It fumes when exposed to moist air, and rapidly deliquesces from absorption of aqueous vapour, and becomes converted into the hydrate, usually called sulphuric acid. Small portions of the anhydride when cautiously thrown into water, occasion each time a hissing sound, and the water gets intensely hot.

The heat must have been stored up in the anhydride and in the water (both cold bodies at the ordinary temperature).

The liquid reddens blue litmus paper most intensely. On distilling the dilute acid in a retort, through the tubulure of which a thermometer is fitted air-tight by means of a soft cork, it yields first water, then hydrated acid, and the boiling-point rises gradually until it remains constant at 326° C. No further change is observed, and the remaining liquid rapidly distils over.

Quantitative experiments have proved that this distillate is a ternary compound of S, O, and H, viz., $SO_4\,H_2$, or SO_3OH_2.

The compound $S^{vi}\,O_3$ is represented graphically:—



$$\begin{array}{c} O \\ \| \\ O{=}S{=}O \end{array}$$

Sulphur being a hexad element. The compound $SO_3\,OH_2$ being, however, a truly chemical compound, the question naturally arises: how are the elements of water connected with the hexad sulphur. If the 6 bonds of the sulphur atom were linked *directly* to the 4 atoms of dyad oxygen, and 2 atoms of monad hydrogen, sulphur would become a decad element ($SO_4\,H_2$).

Now we know that SO_3 can be obtained by the oxidation of SO_2. On passing sulphurous anhydride slowly over plumbic dioxide, PbO_2, loosely spread out in a thin layer in a narrow tube of hard glass, the gas is eagerly absorbed by the binary compound, plumbic dioxide, with which it forms a white compound, called plumbic sulphate, $SO_2\,PbO_2$. The same reaction takes place when manganic oxide, MnO_2, is employed—manganous sulphate, SO_2MnO_2, being formed.

Experiment 55.—Add to a concentrated solution of sulphurous anhydride gas in water, a solution of peroxide* of hydrogen, H_2O_2 (hydric peroxide), until the odour of the sulphurous anhydride gas has entirely disappeared. Sulphurous acid is instantaneously converted into sulphuric acid on coming in contact with hydric peroxide (a compound which is of very great interest, and the formation of which will be described hereafter more fully).

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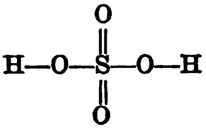
* The prefixes *per*, or *hyper*, are used in cases where the same element forms more than two oxides (acids or bases) with oxygen. More frequently, however, the different oxides are distinguished by the use of the terminals *ous* and *ic*, as manganous, MnO, and manganic oxide, MnO_2, sulphurous, SO_2, and sulphuric anhydride, SO_3.

$$\mathbf{S}O_2 + H_2O_2 = SO_2H_2O_2, \text{ or } \mathbf{S}O_2Ho_2.$$

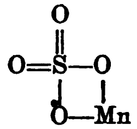
Sulphurous anhydride. Hydric peroxide. Sulphuric acid.

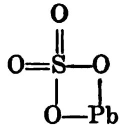
If we then regard the chemical compound which is formed when $\mathbf{S}O_2$ and $\mathbf{O}H_2$ are brought together, as consisting of sulphurous anhydride gas and hydric peroxide, we shall be able to represent it graphically as follows:—



$$\begin{array}{c} O \\ \| \\ H{-}O{-}S{-}O{-}H \\ \| \\ O \end{array}$$

and preserve in this manner the hexad nature of the sulphur atom. Manganous sulphate, containing in the place of the two atoms of hydrogen a dyad element, Mn, and plumbic sulphate, the dyad element, Pb, would then be written graphically—





The compound $\mathbf{S}O_2$ is called sulphurous *anhydride* (from ἀν, *not, without,* and ὕδωρ, *water*), and the compound $\mathbf{S}O_3$, sulphuric anhydride; for oxides which form *acids* when they combine with water, or salts when added to bases, are termed *anhydrides.*

Water is usually viewed as an oxide of hydrogen. It may, however, also be regarded as a hydride of the semi-molecule HO. Many bodies of analogous nature occur among organic compounds, and we are, therefore, perfectly justified in taking this view of water, viz.:—

$$\mathbf{O}H_2 = H\ HO$$

Hydric peroxide being then represented by—

$$H_2O_2 = HO\ HO$$

the compound H_2O_2 consisting of two parts of the binary compound HO, which has not as yet been obtained in an isolated condition, but exists merely in the form of the molecule. One of the semi-molecules, HO, in H_2O_2, takes the place of H in $\mathbf{O}H_2$, and it is, therefore, equivalentic to H; *i.e.*, it possesses the same binding power as hydrogen, or chlorine, or any other monad element. Such a group of elements which is capable of taking the place of one or more atoms of H is termed a *compound radical.* The radical HO has received the name of *hydroxyl,* and is conveniently expressed symbolically with a small o after the H, viz., Ho; it must not be supposed, however, for a moment that a different atomic value appertains to the small o than the large O. Hydric peroxide consists of two parts of the compound radical hydroxyl. Although Ho is a compound, it yet *acts* the part of a simple atom, because it *enters into combination with other atoms, according to definite weight.*

Graphic representation illustrates clearly its monad nature, for we must write hydroxyl—

$$H—O—$$

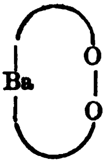
only one hypothetical point of attachment of the oxygen atom being left by which it can join itself to hydrogen to form water, or to another hydroxyl radical to form hydric peroxide.

In like manner there must be as many compound radicals possible as there are metals. A few may be said to correspond to the peroxides, but in most cases they are purely hypothetical creations, as the peroxides of many metals are unknown; thus we have—

Metals.		Oxides.	Peroxides.	Compound radicals corresponding to hydroxyl or its multiple.
Potassium..	K	$\mathbf{O}K_2$	$K_2O_2 = \left\{\begin{array}{l}\mathbf{O}K\\ \mathbf{O}K\end{array}\right.$	Ko (Potassoxyl).
Barium....	Ba″	$\mathbf{Ba}O$	$BaO_2 = \left\{\begin{array}{l}O\\ O\end{array}\right.Ba$	Bao″ (Baroxyl).
Magnesium.	Mg″	$\mathbf{Mg}O$	—	Mgo″ (Magnesoxyl).
Zinc	Zn″	$\mathbf{Zn}O$	—	Zno″ (Zincoxyl).
Iron	Fe″	$\mathbf{Fe}O$	—	Feo″ (Ferrosoxyl).
Lead	Pb″	$\mathbf{Pb}O$	$Pb^{iv}O_2$	Pbo″ (Plumboxyl).
Antimony..	Sb‴	$\mathbf{Sb}_2O_3$	—	Sbo‴ (Antimonoxyl).
Bismuth ..	Bi‴	$\mathbf{Bi}_2O_3$	—	Bio‴ (Bismuthoxyl).

The atoms of oxygen in these compound radicals are represented by a small o, indicating their binding function, as distinct from the O atoms in the peroxides. In the peroxides the oxygen and metal are connected by one bond only of the O atoms, whilst the remaining bonds of the oxygen atoms satisfy each other; this is indicated by bracketing the oxygen atoms. In the metalloxyls, on the other hand, the oxygen atoms are linked to one or more atoms of other elements, for example—

Baric Peroxide $\mathbf{Ba}\left.\begin{array}{l}O\\ O\end{array}\right\}$



Baroxyl ..... Bao″ —O—Ba—O—

The dashes and Roman figures after the small o indicate that the compound radicals, which these metals form, are capable of replacing one, two, three, etc., of the monovalentic radical Ho.

On viewing in like manner the sulphuretted hydrogen gas, $\mathbf{S}H_2$, which we obtained in Experiment 42, we may regard it either as water, $\mathbf{O}H_2$, in which the oxygen atom has been replaced by an atom of sulphur, or as the hydride of a compound radical *hydrosulphyl*, HS, analogous to hydroxyl,—conveniently written with a small s, Hs, after the hydrogen, and represented graphically thus—

H—S—

Only one point of attachment is left open in the dyad atom sulphur by which it can link itself to hydrogen to form sulphuretted hydrogen, or to a monad element, ex. gr., sodium, Na, potassium, K, to form NaHs, KHs.

The ternary chemical compounds which are obtained when water combines with metallic oxides to form *hydrates*, must be expressed graphically in like manner. We may view potassic oxide, $\mathbf{O}K_2$, as composed of the compound radical potassoxyl Ko—the radical in the molecule potassic dioxide $\left(\begin{matrix}\mathbf{O}K\\ \mathbf{O}K\end{matrix} \text{ or } K_2O_2\right)$— together with an atom of K, thus—

$$\mathbf{O}K_2 = KKo;$$

and potassic hydrate as a compound of K and Ho, the radical hydroxyl, Ho, replacing potassoxyl, Ko, in potassic oxide.

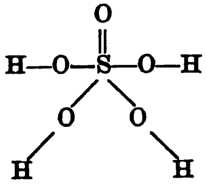
K— —O—K, or K—O—K.
K— —O—H, or K—O—H.

Metallic hydrates, then, may be viewed as binary compounds, in which one, two, three, or four parts of the compound radical hydroxyl are combined with one atom of a metal, according as the latter is of a monad, dyad, triad, or tetrad nature.

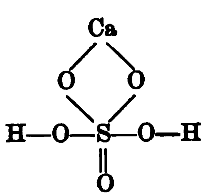
Hydrates of monad metals—	Graphically—
KHo . NaHo . AgHo	K—Ho.
Hydrates of dyad metals—	
$\mathbf{Ca}''Ho_2$. $\mathbf{Fe}''Ho_2$. $\mathbf{Pb}''Ho_2$	$\mathbf{Ca}''{=}Ho_2$.
Hydrates of triad metals—	
$\mathbf{Au}'''Ho_3$. $\mathbf{Sb}'''Ho_3$. $\mathbf{Bi}'''Ho_3$,	$\mathbf{Au}''' \equiv Ho_3$.
Hydrates of tetrad metals—	
$\mathbf{Sn}^{iv}Ho_4$,	$\mathbf{Sn}^{iv} \equiv Ho_4$.

Some of the metallic oxides possess little or no affinity for water, or, if they combine with it, form only weak chemical compounds, which are broken up again on the application of heat, into water, which is given off, and oxides. On the other hand, metallic oxides are often capable of fixing more than one molecule of water; thus potassic hydrate (which is generally sold in the form of sticks, from having been run into cylindrical metallic moulds whilst in an oily condition; or in lumps, from being poured into flat iron vessels and broken up when cold), if left exposed to the air attracts moisture very rapidly, and forms an oily liquid—it *deliquesces.* Oil of vitriol, or sulphuric hydrate (which contains generally a little more than one molecule of water), also attracts moisture very eagerly. It is, therefore, employed for drying gases which are not acted upon by the acid. By passing gases through sulphuric hydrate, contained in a two-necked Woulfe's bottle, they are freed from moisture, and may be collected in a perfectly dry state. As the combination of a further molecule, or number of molecules of water with potassic hydrate or sulphuric hydrate is accompanied by a considerable rise in temperature, it is inferred that several hydrates of one and the same oxide may exist; and this is actually the case. A tetrahydric sulphuric acid, for instance, exists, which boils at 242°C., and is formed from two molecules of water and one of sulphuric anhydride.

Symbol SO_3, $2H_2O$, or $\mathbf{S}OHo_2Ho_2$,



A natural compound, called *gypsum* (dried at 100° C.), is the acid salt of this tetrahydric acid, viz., $\mathbf{S}O\ Ho_2\ Cao''$ (dihydric calcic sulphate).



It is usual to express dilute sulphuric acid by the formula $\mathbf{S}O_2Ho_2$, and a solution of potassic hydrate, or caustic potash, by the formula KHo, without regard to the amount of hydration which these bodies have undergone. The same formulæ, however, possess likewise a definite meaning; expressing, as has been already shown, in the strict sense of our symbolic notation, sulphuric monohydrate, potassic monohydrate.

QUESTIONS AND EXERCISES.

1. Define what is meant by reactions in the *wet* and *dry* way.
2. Give instances of combination between oxides and water, and state on what grounds you consider such compounds to be the result of a *chemical* and not merely physical combination.
3. What do we understand by the terms *ternary* compound, *anhydride*, *peroxide*, *hydroxyl*, *hydrosulphyl*, *deliquescence*?
4. Give symbolic and graphic formulæ of sulphurous and sulphuric anhydride, of diyhdric sulphuric acid, of manganous sulphate, and of dihydric calcic sulphate.
5. Assign reasons for writing the symbolic formula of sulphuric acid, $\mathbf{S}O_2Ho_2$, instead of SO_4H_2.
6. Define a *compound radical*. Give illustrations.
7. Write out the names of the compound radicals, corresponding to hydroxyl, of the following metals:—*sodium*, *calcium*, *copper* (*cuprum*), *mercury*, *silver* (*argentum*). Give symbolic and graphic formulæ.
8. Explain the use of the bracket and of the terminals *ous* and *ic*.
9. Give symbolic and graphic formulæ for baric peroxide, manganic oxide, plumbic dioxide, potassic dioxide, potassic hydrate, calcic hydrate, stannic hydrate, baroxyl, plumboxyl, argentic peroxide, argentoxyl, antimonious hydrate.
10. You have given to you quicklime, dilute sulphuric acid, and water; what chemical combinations are you able to produce with these materials?
11. Calculate the percentage composition of baric peroxide.
12. What is the percentage of water in calcic hydrate, and in monohydrated sulphuric acid?

CHAPTER XII.

HYDROCHLORIC ACID.—CONVERSION OF METALLIC OXIDES INTO CHLORIDES.—OXIDES OF CHLORINE.

Experiment 56.—A flask fitted with a cork and delivery-tube, is charged with a few pieces of fused sodic chloride; oil of vitriol is added in sufficient quantity to cover the salt. On gently heating, a colourless gas is evolved, which, on coming in contact with the air, fumes considerably (comp. Exp. 52).

The reaction is expressed by the equation—

$$Na\,Cl + \mathbf{S}O_2Ho_2 = \underset{\text{Hydric sodic sulphate.}}{\mathbf{S}O_2HoNao} + HCl.$$

Hydrochloric acid gas can be obtained perfectly anhydrous by passing it through a Woulfe's bottle containing pieces of pumice-stone, moistened with oil of vitriol (as was shown in Fig. 46), and can then be collected by *displacement*. For this purpose pass the delivery-tube to the bottom of a perfectly dry globular flask. The lighter air is gradually lifted out of the flask by the heavier gas (the sp. gr. of HCl being 1·247, as compared with air), and its escape from the flask is marked by white fumes, produced by the combination of the otherwise transparent gas with the moisture of the air.

Hydrochloric acid gas possesses a powerful attraction for water.

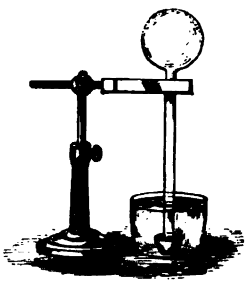


FIG. 47.

In order to illustrate this, place the globular flask with its mouth downwards in a small capsule full of mercury. Transfer cautiously to a basin of water (Fig. 47), coloured blue by a few drops of litmus, and open the flask under water by raising its mouth out of the mercury. The water rushes in with great violence, for it is capable of absorbing 480 times its bulk of hydrochloric acid gas. The blue colour changes instantaneously to red.

Experiment 57.—Pass a slow current of dry hydrochloric acid gas directly from the drying-bottle over freshly ignited cupric oxide, $\mathbf{Cu}O$, placed in a porcelain boat inside a tube of hard glass, in a manner similar to that shown in Fig. 23. The copper lays hold of the chlorine, and the oxygen combines with the hydrogen, according to the equation—

$$\mathbf{Cu}O + 2HCl = \mathbf{Cu}Cl_2 + \mathbf{O}H_2.$$

The water is carried along and partly condensed in the further part of the tube, or carried with the undecomposed hydrochloric acid into a bottle containing a solution of sodic hydrate. The black oxide of copper is converted into a greenish liquid, which is partly left in the boat, and partly volatilized and condensed with a portion of the water. The reaction takes place in the cold, but much more rapidly when the part of the tube containing the boat is gently heated. On allowing it to cool, and dissolving the cupric chloride left in the boat by the addition of a little water, a green solution is obtained.

The same change takes place when mercuric or zincic oxide is acted upon, according to the equation—

$$\mathbf{Hg}O + 2HCl = \mathbf{Hg}Cl_2 + \mathbf{O}H_2,$$
$$\mathbf{Zn}O + 2HCl = \mathbf{Zn}Cl_2 + \mathbf{O}H_2,$$

water being invariably produced, whilst metallic chlorides are formed.

A solution of hydrochloric acid gas in water (sometimes called spirit of salt, muriatic acid, chlorhydric acid, and hydric chloride), is largely used in the laboratory, and constitutes one of the most indispensable reagents.

Experiment 58.—Put one part by weight of dry sodic chloride (common salt), and two parts by weight of concentrated sulphuric acid (previously diluted with one-third of water) in a flask (Fig. 41), shake well up, connect with two or three Woulfe's bottles, and apply a gentle heat. Small quantities of sulphuric acid, which may be carried over, are arrested in the first Woulfe's bottle. The delivery-tubes should be adjusted so as to dip barely into the water, because the hydrochloric acid is so eagerly absorbed by the water as to cause the contents of the Woulfe's bottles to recede, and because the acid liquid which is formed, being heavier than water, sinks rapidly to the bottom.

A solution of pure hydrochloric acid should be quite colourless.

Experiment 59.—Take a dilute solution of caustic soda (sodic hydrate) and add to it a few drops of litmus solution. The liquid turns intensely blue. Add now, by means of a little pipette (Fig. 48), dilute hydrochloric acid, drop by drop, and keep stirring with a glass rod. Each drop of acid causes the blue liquid to turn red, wherever it falls. The red disappears, however, on agitating the liquid; but as soon as the greater portion of the alkali has combined with the acid, the red colour disappears more slowly; and one single drop of acid at last turns the whole of the blue liquid permanently red.

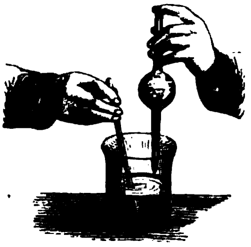


Fig. 48.

This is a sign that no more free or uncombined alkali is left. The alkali is *saturated* with acid; as it is termed, it is *neutralized*, *i.e.*, it does not affect either blue or red litmus. The chemical combination between sodic hydrate and hydrochloric acid is accomplished according to the equation—

$$NaHo + HCl = NaCl + \mathbf{O}H_2.$$

Chlorine possesses a strong affinity for the metal sodium. It leaves the hydrogen and combines with sodium to form *common salt or sodic chloride*, NaCl, which crystallises out on evaporation in a porcelain dish. Pour off the liquid and spread the crystals on filter paper, placed on a porous tile, to dry.

It follows from this experiment that a metallic chloride can be obtained also by neutralizing a solution of a metallic hydrate with dilute hydrochloric acid, and that such chlorides possess all the properties of chlorides obtained in the dry way.

Metallic chlorides can, with few exceptions, be prepared, as we have hitherto* seen,

1. *By the direct combination of chlorine with metals* (comp. Exps. 48, 49, and 50), *e.g.*,

$$\mathbf{M}g + Cl_2 = \mathbf{M}gCl_2.$$

2. *By the action of hydrochloric acid, either in the gaseous form or as dilute acid, upon metals* (comp. Exps. 2 and 52), *e.g.*,

$$Na_2 + \underset{\text{Gaseous.}}{2HCl} = 2NaCl + H_2.$$

$$\mathbf{Zn} + \underset{\substack{\text{A dilute}\\\text{solution.}}}{2HCl} = \mathbf{Zn}Cl_2 + H_2.$$

3. *By the action of hydrochloric acid, no matter whether as gas or in solution, upon metallic oxides* (comp. Exp. 57), *e.g.*,

$$\mathbf{Cu}O + 2HCl = \mathbf{Cu}Cl_2 + \mathbf{O}H_2.$$

4. *By the action of dilute hydrochloric acid upon metallic hydrates* (comp. Exp. 59), *e.g.*,

$$KHo + HCl = KCl + \mathbf{O}H_2.$$

---

* Other modes of forming metallic chlorides will be dealt with below.

Methods 3 and 4, of preparing chlorides, moreover, are the most convenient and most generally adopted, since metallic oxides or hydrates, which occur more frequently in nature than the metals, are much more easily and cheaply converted into chlorides than the metals themselves. This applies especially to the lighter metals, Na, K, Ba, Sr, Ca, Mg, Al.

We can prepare in this manner *potassic chloride*, *baric*, and *calcic chloride*, etc., by neutralizing their corresponding hydrates with dilute hydrochloric acid, according to the equations—

$$\begin{aligned} KHo &+ HCl = KCl + \mathbf{O}H_2, \\ \mathbf{Ba}Ho_2 &+ 2HCl = \mathbf{Ba}Cl_2 + 2\mathbf{O}H_2, \\ \mathbf{Ca}Ho_2 &+ 2HCl = \mathbf{Ca}Cl_2 + 2\mathbf{O}H_2. \end{aligned}$$

Solutions thus obtained are termed *chemical* solutions, because the solvent, HCl, forms with the dissolved substance a chemical compound.

All metallic chlorides, with the exception of argentic, mercurous, and plumbic chloride, are soluble in water; the latter is, however, partially soluble in cold, and readily soluble in boiling water.

It may be useful to examine for a moment somewhat more closely into the action of hydrochloric acid upon the more important metals (method 2), and to observe—

1. *That certain metals*[*] *are readily dissolved with evolution of hydrogen*, viz., K', Na', Ba'', Sr'', Ca'', Mg'', Al^{iv}, $\mathbf{Fe}''$, $\mathbf{Zn}''$, Cd'', Ni'', Co'', and (pulverulent) Cr^{iv}.
2. *Others are only with difficulty soluble in boiling acid*, viz., $\mathbf{Sn}''$.
3. *Others again are but slightly attacked by hydrochloric acid*, viz., Sb''', Pb'', Ag', Bi''', Cu'', and
4. *A few metals are not affected either by cold or hot hydrochloric acid*, viz., Au, Pt, As, Hg, and (crystalline) Cr.

Hydriodic, hydrobromic, and hydrofluoric acid act in a similar manner upon metallic hydrates. They form iodides, bromides, and fluorides, ex. gr.—

$$\begin{aligned} KHo &+ HI = KI + \mathbf{O}H_2 \\ \mathbf{Mg}Ho_2 &+ 2HBr = \mathbf{Mg}Br_2 + 2\mathbf{O}H_2 \\ NaHo &+ HF = NaF + \mathbf{O}H_2. \end{aligned}$$

All metallic iodides and bromides, with the exception of argentic iodide and bromide, are soluble in water. Metallic fluorides, on the other hand, are for the most part insoluble in water, with the exception of the alkaline and a few other fluorides. The best known fluoride is calcic fluoride, or *fluor spar*, insoluble in water and dilute acids.

---

[*] Practically no other but the few metals printed in thick type would ever be thus used for the preparation of metallic chlorides. The atomicity marks placed on the right hand side above the symbols indicate the nature of the chlorides which the different metals form under the given circumstances.

Compounds of Chlorine with Oxygen.—There is no method known by which chlorine can be made to unite directly with oxygen. The consideration of the more important compounds formed by chlorine with different proportions of oxygen, as set forth in the following table, will, therefore, be resumed when the reactions of the oxy-acids of chlorine come to be studied.

Oxides of Chlorine.

Name.	Symbolic Formulæ.	By weight.	
		Cl	O
Hypochlorous anhydride......	$\mathbf{O}\mathrm{Cl}_2$	71	16
Chloric oxide (?)	$\left\{\begin{matrix}\mathbf{O}\mathrm{Cl}\\ \mathbf{O}\mathrm{Cl}\end{matrix}\right\}$	71	32
Chlorous anhydride	$\left\{\begin{matrix}\mathbf{O}\mathrm{Cl}\\ \mathrm{O}\\ \mathbf{O}\mathrm{Cl}\end{matrix}\right\}$	71	48
Chloric peroxide	$\left\{\begin{matrix}\mathbf{O}\mathrm{Cl}\\ \mathrm{O}\\ \mathrm{O}\\ \mathbf{O}\mathrm{Cl}\end{matrix}\right\}$	71	64
Chloric hyperoxide (?)	$\left\{\begin{matrix}\mathbf{O}\mathrm{Cl}\\ \mathrm{O}\\ \mathrm{O}\\ \mathrm{O}\\ \mathrm{O}\\ \mathbf{O}\mathrm{Cl}\end{matrix}\right\}$	71	96

QUESTIONS AND EXERCISES.

1. How would you demonstrate the great solubility of hydrochloric acid gas in water ?
2. What is the action of dry HCl gas upon dry metallic oxides ? Give equations.
3. How is a concentrated solution of hydrochloric acid prepared ?
4. You have given to you a dilute solution of sodic hydrate and dilute hydrochloric acid : state how you would prepare from these materials crystals of common salt ?
5. Explain the terms *neutralize, chemical solution, evaporation.*
6. Which metallic chlorides are insoluble in water ?
7. Commit to memory the action of hydrochloric acid upon the more important metals.
8. Enumerate the different methods for preparing metallic chlorides, and state which methods you would follow if you had to prepare cupric chloride, mercuric chloride, zincic and ferrous chloride, sodic chloride, stannous chloride. Give equations.

9. Give symbolic and graphic formulæ for antimonious, cupric, magnesic, cobaltous, manganous, and argentic chlorides.
10. How much sulphuric acid (SO_2Ho_2, molecular weight 98) is required to decompose 100 grms. of fused sodic chloride, so as to leave hydric sodic sulphate?
11. How much metallic zinc can be dissolved by 50 grms. of hydrochloric acid containing 20 per cent. of acid by weight.
12. How much dry hydrochloric acid gas by weight and by volume will be required to combine with 5 grms. of ignited cupric oxide?

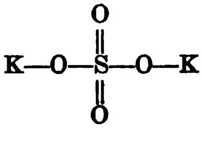
CHAPTER XIII.

FORMATION OF TERNARY OXY-COMPOUNDS FROM METALLIC HYDRATES AND OXY-ACIDS. —CARBONIC AND SULPHUROUS ACID.—CARBONATES, SULPHATES, AND SULPHITES.

Experiment 60.—An aqueous solution of caustic potash (potassic hydrate) is neutralized, as shown in Experiment 59, in a beaker with moderately dilute sulphuric acid (1 part by measure of strong acid diluted with 3 parts by measure of water). A few drops of litmus solution are added to indicate the change from blue to red, *i.e.*, the neutralization of the alkali by the acid. The liquid is evaporated in a porcelain dish till a slight film forms upon it and then set aside to cool. Crystals of a salt called ***potassic sulphate*** are obtained. The change takes place according to the equation—

$$2KHo + SO_2Ho_2 = SO_2Ko_2 + 2OH_2.$$

On examining the crystals quantitatively, they are found to be composed of K, S, and O only, water being eliminated. By the change, the compound radical potassoxyl, Ko, takes the place of the radical Ho, or a molecule of potassoxyl, Ko_2, replaces the molecule Ho_2 in sulphuric acid. It is represented graphically thus:—



$$\begin{array}{c} O \\ \| \\ K—O—S—O—K \\ \| \\ O \end{array}$$

We have already become acquainted with a gaseous compound of carbon and oxygen, called carbonic anhydride gas, CO_2, which we obtained by burning carbon in air or oxygen. This gas is more readily prepared by acting upon mineral bodies containing it, such as chalk, marble, with hydrochloric or other acid.

Experiment 61.—Introduce into a bottle (Fig. 49) a few pieces of marble and add through the funnel-tube dilute hydrochloric acid. Effervescence ensues and a colourless gas comes off. Fresh acid is added from time to time, as long as any marble is left undissolved. The reaction is expressed by the equation—

$$\mathbf{C}OCao'' + 2HCl = \mathbf{Ca}Cl_2 + \mathbf{C}O_2 + \mathbf{O}H_2.$$

Calcic carbonate. Calcic chloride.

We can readily collect some of the gas over water in glass cylinders and have no difficulty in recognising it as carbonic anhydride, since it extinguishes a light, is heavier than air, and gives a white precipitate with lime or baryta water. Its specific gravity compared with air is 1·529 or $\frac{1{\cdot}529}{{\cdot}0693} = 22$, when compared with hydrogen. 1 litre of the two-volume vapour carbonic anhydride, consisting of one atom of carbon and two atoms of oxygen weighs $\frac{12 + 2 \times 16}{2} = 22$ times as much as a litre of hydrogen or 22 criths, *i.e.*, 22 × ·0896 grm. = 1·9712 grm. The molecular weight of carbonic anhydride is therefore 44. It is written graphically $O = C = O$, carbon being a tetrad element.

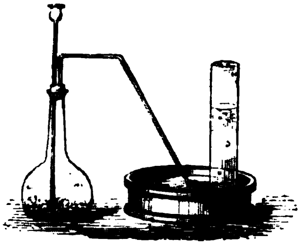
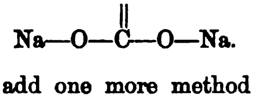


FIG. 49.

Experiment 62.—Pass some carbonic anhydride into a solution of caustic soda, NaHo. The gas is absorbed. On evaporating the solution to dryness, and igniting gently in a porcelain dish, then dissolving the dry mass once more in hot water, crystals of a salt are obtained, which analysis has shown to be composed of three elementary bodies, viz., sodium, carbon and oxygen. Its formation is explained by the following equation:—

$$2NaHo + \mathbf{C}O_2 = \mathbf{C}ONao_2 + \mathbf{O}H_2.$$

The salt is disodic carbonate, and is one of a large and important class of salts called *carbonates*. The tetrad element carbon forms the grouping element, its bonds being satisfied by one atom of dyad oxygen and two parts of the monad radical sodoxyl, Nao. It is expressed graphically:—



$$Na{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}Na.$$

We have now to add one more method to the four methods enumerated above for preparing metallic chlorides, viz., *by the action of dilute hydrochloric acid upon metallic carbonates, e.g.*—

$$\mathbf{C}\mathrm{OCuo}'' + 2\mathrm{HCl} = \mathbf{Cu}\mathrm{Cl}_2 + \mathbf{C}\mathrm{O}_2 + \mathbf{O}\mathrm{H}_2$$
$$\mathbf{C}\mathrm{OMgo}'' + 2\mathrm{HCl} = \mathbf{Mg}\mathrm{Cl}_2 + \mathbf{C}\mathrm{O}_2 + \mathbf{O}\mathrm{H}_2.$$

It is obvious *that metallic sulphates* (comp. Exp. 60) *may*, in like manner, *be prepared from metallic carbonates, by treating the latter with dilute sulphuric acid, e.g.*—

$$\underset{\text{Ferrous carbonate.}}{\mathbf{C}\mathrm{OFeo}''} + \mathbf{S}\mathrm{O}_2\mathrm{Ho}_2 = \underset{\text{Ferrous sulphate.}}{\mathbf{S}\mathrm{O}_2\mathrm{Feo}''} + \mathbf{C}\mathrm{O}_2 + \mathbf{O}\mathrm{H}_2,$$

and as many metals occur in nature abundantly in the form of carbonates (*e.g.*, K, Na, Ba, Sr, Ca, Mg, Fe, Zn, Mn, Pb, Cu), this method of preparing chlorides and sulphates will at once recommend itself as the most convenient and cheapest, especially as carbonates are, for the most part, decomposed with great facility even by weak organic acids, such as acetic or tartaric acid.

Experiment 63.—Pass carbonic anhydride gas through a solution of baric hydrate, BaHo_2. The gas is likewise absorbed, and a white precipitate falls as soon as the first bubbles of the gas are passed into the solution. The precipitation ceases after a while, and by filtering off the white powder, which consists of barium, carbon and oxygen, we obtain a salt called baric carbonate, which is insoluble in water. Its formation is expressed by the equation:—

$$\mathbf{Ba}\mathrm{Ho}_2 + \mathbf{C}\mathrm{O}_2 = \mathbf{C}\mathrm{OBao}'' + \mathbf{O}\mathrm{H}_2.$$

On passing carbonic anhydride gas somewhat longer through the solution in which some of the precipitate is suspended, the precipitate disappears and the liquid becomes once more clear. Excess of carbonic anhydride then dissolves the baric carbonate; it combines in fact with the caustic alkalies and alkaline earths in two proportions, forming either a neutral carbonate or an acid, or hydric carbonate respectively.

The carbonates of the alkali metals are soluble in water, all other carbonates are insoluble.

Potassic sulphate, like sodic chloride, has neither acid nor basic properties; it is an indifferent body. Sulphates of the alkali metals are soluble in water. Baric sulphate is practically insoluble in water as well as in dilute acids; strontic, calcic, and plumbic sulphates are nearly so, argentic sulphate is difficultly soluble in water. All other metallic sulphates are soluble in water.

Metallic sulphates can, with few exceptions, be prepared—

1st. *By the action of sulphuric acid upon the metals*,*

(*a*) *with evolution of hydrogen*, *e.g.*, K, Na, Ba, Sr, Ca (the last three metals are imperfectly acted upon on account of the formation of insoluble sulphates). Mg, Al (requires the application of heat) **Fe**″, **Zn**″, Cd, Ni, Co, Mn, and (pulverulent) Cr, Sn (imperfectly acted upon by dilute sulphuric acid with evolution of hydrogen).

(*b*) *by the action of concentrated sulphuric acid with evolution*

---

* Practically no others than the metals printed in thick type would ever be dissolved in sulphuric acid for the purpose of preparing their sulphates.

sulphurous anhydride ($\mathbf{S}O_2$) especially on heating, *e.g.*, $\mathbf{Cu}''$, $\mathbf{Bi}'''$ $\mathbf{Hg}''$ $\mathbf{Ag}'$, $\mathbf{Sb}'''$ and $\mathbf{Sn}''$, Pb (slightly soluble only on heating.)

whilst a few metals, such as Au, Pt, As and Cr (crystalline) are not affected by concentrated sulphuric acid.

2nd. *By the action of dilute sulphuric acid upon metallic oxides, e.g.*—

$$\underset{\text{Zincic oxide.}}{\mathbf{Zn}O} + \mathbf{S}O_2Ho_2 = \underset{\text{Zincic sulphate.}}{\mathbf{S}O_2Zno''} + \mathbf{O}H_2.$$

3rd. *By the action of dilute sulphuric acid upon metallic hydrates, e.g.*—

$$\underset{\text{Manganous hydrate.}}{\mathbf{Mn}Ho_2} + \mathbf{S}O_2Ho_2 = \underset{\text{Manganous sulphate.}}{\mathbf{S}O_2Mno''} + \mathbf{O}H_2.$$

4th. *By the action of dilute sulphuric acid upon metallic carbonates,* as described above.

Experiment 64.—Introduce some copper clippings into a flask, fitted with a funnel and delivery-tube (as seen in preceding fig.). Add a little concentrated sulphuric acid, and heat gently over a sand-bath. A gas is evolved, which is readily recognized by its pungent odour as *sulphurous anhydride.* The reaction takes place according to the equation:—

$$Cu + 2\mathbf{S}O_2Ho_2 = \underset{\text{Sulphurous anhydride.}}{\mathbf{S}O_2} + \underset{\text{Cupric sulphate.}}{\mathbf{S}O_2Cuo''} + \mathbf{O}H_2.$$

The oxidation of the copper is effected at the expense of sulphuric acid with evolution of one molecule of $\mathbf{S}O_2$. A second molecule of $\mathbf{S}O_2Ho_2$ combines with the cupric oxide to form cupric sulphate, which is left behind in the flask and which may be recovered by dissolving in water, filtering and evaporating, in the form of fine blue crystals ($\mathbf{S}O_2Cuo'',5\mathbf{O}H_2$).

Several other metals, *e.g.*, Hg, Ag, might have been substituted for the metallic copper.

When sulphurous anhydride is absorbed by water it produces sulphurous acid, $\mathbf{S}OHo_2$, thus:—

$$\mathbf{S}O_2 + \mathbf{O}H_2 = \mathbf{S}OHo_2.$$

Sulphurous anhydride, when passed into a solution of sodic hydrate, is absorbed with formation of a *sulphite*, if the $\mathbf{S}O_2$ be in excess—of an *acid* sulphite, *e.g.*,—

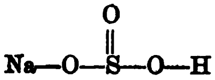
$$2NaHo + \mathbf{S}O_2 = \mathbf{S}ONao_2 + \mathbf{O}H_2.$$

$$NaHo + \mathbf{S}O_2 = \underset{\text{Acid or hydric sodic sulphite.}}{\mathbf{S}OHoNao.}$$

Metallic sulphites are readily produced by adding a solution of sulphurous acid to a metallic hydrate, oxide, or carbonate. The grouping element sulphur acts as a tetrad element. Its bonds are satisfied in metallic sulphites by one atom of dyad O and two of a monad or one of a dyad metalloxyl, thus:—

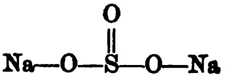
Symbolically. *Graphically.*

$\mathbf{S}\mathrm{OHoNao}$



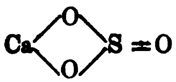
$\mathrm{Na{-}O{-}\overset{\overset{O}{\|}}{S}{-}O{-}H}$

$\mathbf{S}\mathrm{ONao_2}$



$\mathrm{Na{-}O{-}\overset{\overset{O}{\|}}{S}{-}O{-}Na}$

$\mathbf{S}\mathrm{OCao''}$



Sulphurous anhydride (like carbonic anhydride) is readily liberated from metallic sulphites by the action of hydrochloric, or sulphuric acid.

Potassic sulphate is the representative of a large number of ternary compounds called *oxy-salts*, because three elementary bodies enter into their composition, one of which is always oxygen.

Salts may thus be divided into—

1. *Haloid salts* (binary compounds), *e.g.*, chlorides, bromides, iodides, etc.
2. *Oxy-salts* (ternary compounds), *e.g.*, sulphates, sulphites, carbonates, etc.

and the same nomenclature is used in the case of oxy-salts which was adopted for haloid salts, viz., the name of the metallic element is employed adjectively, and that of the acid substantively; the name of the acid element of oxy-salts ending, however, as in potassic sulphate and sodic sulphite in *ate* and *ite*, in order to distinguish them from the acid element of haloid salts which terminate in *ide*, as potassic chloride.

QUESTIONS AND EXERCISES.

1. You have given to you metallic silver, ferrous carbonate and sulphuric acid. State what chemical compounds can be produced from these materials. Express the changes by equations.
2. Describe the most convenient methods for preparing magnesic sulphate, disodic sulphite, mercuric and zincic sulphate. Express the changes by equations.
3. Explain what takes place when $\mathbf{C}O_2$ is successively passed into distilled water, into solutions of baric or calcic hydrate.
4. Find the volume weight of $\mathbf{C}O_2$, and calculate the weight of 66·5cc. of carbonic anhydride.
5. You have given to you a piece of charcoal weighing 5 grms. and 6 litres of oxygen. How much $\mathbf{C}O_2$ by volume and by weight can you obtain by the combustion of the carbon in oxygen, and how much carbon, if any, will be left?

6. How much CO_2 by weight and by volume will be required to convert 2·5 grms. of NaHo into disodic carbonate?
7. Give the symbolic and graphic formulæ of the following compounds: sulphurous acid, hydric sodic sulphite, baric carbonate, calcic sulphate, magnesic sulphite.
8. Explain what nomenclature has been adopted for distinguishing haloid from oxy-salts. Give illustrations.
9. We inhale air and throw off carbonic anhydride from our lungs. How would you show experimentally that the amount of CO_2 in a given volume of air which comes from our lungs, is far greater, than the quantity of carbonic anhydride which is found in an equal volume of the air which we inhale.

Chapter XIV.

THE OXIDES OF NITROGEN.

Two important compounds containing one of the oxides of nitrogen in combination with the alkali metals potassium and sodium exist in nature, and are known to us as *potash nitre* (or *saltpetre*) and *soda nitre* (*Chili saltpetre*, *cubic nitre*). The affinity which nitrogen possesses for oxygen is so feeble, that in atmospheric air (which consists of a mixture of these two gases) they exist side by side without combining; and it is only by the most powerful agencies (such as electrical discharges) that very trifling quantities of an acid product of oxidation can be obtained. Nitre is principally found in tropical countries, where the rapid oxidation of certain organic nitrogenized bodies, such as animal excrements and especially urine, under the influence of a hot tropical sun, especially in presence of porous lime soils and soils rich in alkalies, produces this most important of nitrogen compounds in considerable quantities. We know of no reactions by which the oxides of nitrogen could be formed directly from their elements in appreciable quantities. The affinity which draws their component atoms together being found very feeble, their power of resisting decomposition is proportionally weak; and hence it is that these compounds part readily with their oxygen, and that the different oxides of nitrogen are among the most powerful *oxidizing* agents known.

Experiment 65.—Introduce into a small retort (Fig. 50) a little nitre with sufficient concentrated sulphuric acid to cover the salt. Carefully prevent the acid and the salt from coming in contact with the neck of the retort.

Apply gentle heat. A reaction is seen to take place, and ruddy vapours come off which condense in the neck of the retort. The receiving flask should be kept cool by partially immersing it in a basin of cold water and by covering it with a wet cloth or filter-paper. The distillation continues briskly for

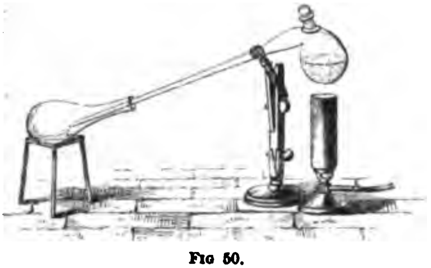
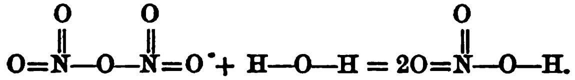


FIG 50.

some time, and an orange red liquid condenses in the receiver. The operation may be discontinued when no more ruddy vapours are observed in the body and neck of the retort.

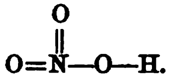
The liquid in the receiving flask reddens blue litmus instantaneously. It is an acid body called nitric acid. Analysis has proved that it is a ternary body, composed of nitrogen, oxygen and hydrogen, viz., N,O_3,H. Nitrogen being, however, a pentad element, it follows that in $2NO_3H$ (which we may view as obtained by the combination of one molecule of N_2O_5 with one molecule of $\mathbf{O}H_2$) six atoms of dyad oxygen and two atoms of monad hydrogen cannot be united directly to two atoms of nitrogen; but that the two atoms of hydrogen link themselves to two atoms of oxygen to form two semimolecules of the compound radical hydroxyl. This may be shown graphically as follows:—



$$O{=}\overset{\overset{\textstyle O}{\|}}{N}{-}O{-}\overset{\overset{\textstyle O}{\|}}{N}{=}O + H{-}O{-}H = 2O{=}\overset{\overset{\textstyle O}{\|}}{N}{-}O{-}H.$$

one molecule of anhydrous $\mathbf{N}_2O_5$ must therefore give rise to two molecules of nitric hydrate or nitric acid, the atom group NO_2 remaining unchanged, like the group SO_2, in $\mathbf{S}O_2Ho_2$.

The pentad element nitrogen links together two atoms of dyad oxygen and the monad radical hydroxyl, and we therefore write the graphic formula of nitric hydrate or nitric acid—



$$O{=}\overset{\overset{\textstyle O}{\|}}{N}{-}O{-}H.$$

The distillate collected in the receiving flask consists of a more or less concentrated solution of nitric acid. It attracts moisture from the air and holds it chemically combined, yielding it up again only by round-about processes, and not without suffering partial decomposition.

On warming the flask ruddy fumes of a suffocating and poisonous nature are given off, and the remaining liquid becomes colourless or nearly so. The volatile gaseous portion consists of lower oxides of nitrogen. It is evident therefore that the affinity which nitrogen possesses for oxygen in nitric acid is not sufficient even to resist its partial decomposition by simple distillation.

The liquid remaining in the retort solidifies on cooling to a saline crystalline mass of hydric potassic sulphate. It is possible under given conditions, *e.g.*, excess of acid, to obtain a sulphate in which only half the Ho is replaced by Ko. Such salts are called *acid* salts. Only dibasic or dihydric acids are capable of forming acid salts. Monobasic acids (such as nitric acid), containing one replaceable Ho, can only form one kind of salts.

The action of sulphuric acid upon nitre or potassic nitrate is expressed by the equation—

$$\mathbf{N}O_2Ko + \mathbf{S}O_2Ho_2 = \mathbf{N}O_2Ho + \mathbf{S}O_2HoKo.$$

Hydric potassic
sulphate.

A more dilute nitric acid formed from one molecule of $\mathbf{N}_2O_5$, and four molecules of water is a much more stable liquid. The degree of hydration in the case of nitric acid, as in that of other acids, is generally not expressed by the formula assigned to the dilute acid.

Nitric acid forms with metallic oxides, hydrates, or carbonates, salts called *nitrates*,* which are all *soluble in water*, ex. gr.

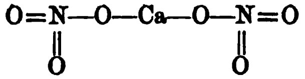
$$\mathrm{KHo} + \mathbf{N}\mathrm{O_2Ho} = \mathbf{N}\mathrm{O_2Ko} + \mathbf{O}\mathrm{H_2}.$$

$$\mathbf{Ca}\mathrm{Ho_2} + 2\mathbf{N}\mathrm{O_2Ho} = \begin{matrix}\mathbf{N}\mathrm{O_2}\\ \mathbf{N}\mathrm{O_2}\end{matrix}\mathrm{Cao''} + 2\mathbf{O}\mathrm{H_2}.$$

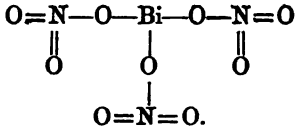
$$\mathbf{Pb}\mathrm{O} + 2\mathbf{N}\mathrm{O_2Ho} = \begin{matrix}\mathbf{N}\mathrm{O_2}\\ \mathbf{N}\mathrm{O_2}\end{matrix}\mathrm{Pbo'} + \mathbf{O}\mathrm{H_2}$$

$$\mathbf{Bi}_2\mathrm{O_3} + 6\mathbf{N}\mathrm{O_2Ho} = 2\begin{pmatrix}\mathbf{N}\mathrm{O_2}\text{—}\\ \mathbf{N}\mathrm{O_2Bio'''}\\ \mathbf{N}\mathrm{O_2}\text{—}\end{pmatrix} + 3\mathbf{O}\mathrm{H_2}.$$

In the calcium and lead salts two molecules of nitric acid are united by the dyad compound radicals Cao″, Pbo″, in the bismuth salt three molecules of acid are held together by the triad compound radical Bio‴. These salts are represented graphically thus:—



$$\begin{matrix}O{=}N{-}O{-}Ca{-}O{-}N{=}O\\ \Vert \qquad\qquad\quad \Vert\\ O \qquad\qquad\quad O\end{matrix}$$



$$\begin{matrix}O{=}N{-}O{-}Bi{-}O{-}N{=}O\\ \Vert \quad\ \ | \quad\ \ \Vert\\ O \quad\ \ O \quad\ \ O\\ |\\ O{=}N{=}O.\end{matrix}$$

Experiment 66.—Heat a small quantity of dry plumbic nitrate (powdered) in a retort of hard glass. Connect the neck of the retort with a U-tube surrounded with cold water, or better still, with a freezing mixture of ice and salt. The lead salt melts and decomposes. Ruddy fumes of nitric peroxide come off, which condense in the U-tube. Oxygen escapes through the open drawn-out end of the tube. Test the gas with a glowing chip of wood; the wood is rekindled. Collect a little over water by attaching a delivery tube to the U-tube.

A dark brown powder is left in the retort, turning orange-yellow on cooling. It consists of plumbic oxide, $\mathbf{Pb}O$. The decomposition may be expressed by the equation—

$$\begin{matrix}\mathbf{N}\mathrm{O_2}\\ \mathbf{N}\mathrm{O_2}\end{matrix}\mathrm{Pbo''} = \mathbf{Pb} + \left\{\begin{matrix}\mathbf{N}\mathrm{O_2}\\ \mathbf{N}\mathrm{O_2}\end{matrix}\right. + \mathrm{O}.$$

This experiment proves—

1. That plumbic nitrate is converted by heat into plumbic oxide.
2. That nitric anhydride, $\mathbf{N}_2O_5$, is given off, but that it breaks up immediately into oxygen, and a gas of a ruddy colour, $\mathbf{N}_2O_4$ or nitric peroxide which can be condensed to a liquid.

Quantitative measurement of the oxygen evolved from a given quantity of plumbic nitrate has proved that it forms exactly ⅕ of the total oxygen contained in nitric anhydride, and the breaking up of the molecule must therefore take place according to the equation:—

---

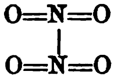
* The action of nitric acid upon metals will be explained below.

$$\mathbf{N}^{v}_2O_5 = \mathbf{N}_2O_4 + O;$$

and as the N_2 in $\mathbf{N}_2O_4$ forms a chemical compound with O_4, it is obvious that the nitrogen atom could no longer be pentavalentic, as four atoms of dyad oxygen can no longer satisfy the combining powers of two atoms of pentad nitrogen. It is also apparent that if nitrogen acted as a tetrad element in $\mathbf{N}_2O_4$, there would be no connection between the two atoms of nitrogen, thus:—

$$\begin{matrix} O{=}N{=}O \\ O{=}N{=}O. \end{matrix}$$

It is therefore probable that the connection between the two nitrogen atoms still exists, even without the intervening oxygen atom, and that nitrogen retains its pentad nature, thus:—



$$\begin{matrix} O{=}N{=}O \\ | \\ O{=}N{=}O \end{matrix}$$

The fact that the atom of oxygen which linked together the two groups of NO_2 in $\mathbf{N}_2O_5$ is so easily driven out by heat, shows—

3. That a marked difference exists between the chemical affinity which the two atoms of nitrogen in $\mathbf{N}_2O_5$ exhibit for the different atoms of oxygen.

The yellow liquid collected in the U-tube boils at 22° C., and solidifies to a mass of colourless crystals at − 13° C. The crystals dissolve at first to a colourless liquid, which turns yellow as the temperature rises and becomes at last red. Blue litmus-paper is turned red by the puffs of ruddy vapour expelled from the liquid; and the compound N_2O_4 was therefore thought to be an acid body, and was called hyponitric acid. This reddening of the litmus is, however, due to the water in the paper, with which $\mathbf{N}_2O_4$ undergoes a decomposition, and the name *hyponitric acid* is quite inappropriate. A most interesting change takes place when the ruddy vapour of $\mathbf{N}_2O_4$ is passed into a solution of potassic hydrate. Complete absorption of the gas is observed to take place, and the liquid loses its alkaline properties. On examining the products thus formed, we find two different salts, potassic nitrate, $\mathbf{N}O_2Ko$, and potassic nitrite, of the composition $\mathbf{N}OKo$. The acid corresponding to this latter salt is $\mathbf{N}OHo$, containing one atom of oxygen less than nitric acid. It is called *nitrous acid*. The change may be expressed by the equation—

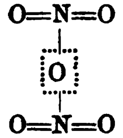
$$\left\{\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}\right. + 2KHo = \mathbf{N}O_2Ko + \mathbf{N}OKo + \mathbf{O}H_2.$$

Nitrous acid, on combining with bases forms well characterised salts called *nitrites*. In the free state, however, it is extremely unstable. It cannot be preserved at the ordinary temperature, without undergoing decomposition, according to the equation:—

$$3\mathbf{N}OHo = \mathbf{N}O_2Ho + \mathbf{N}_2O_2 + \mathbf{O}H_2.$$

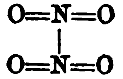
The following considerations render it probable that three atoms of oxygen in nitric anhydride are held less firmly by the nitrogen atoms than the other two atoms of oxygen.

In the molecule of nitric anhydride represented graphically by the formula—



$$\begin{array}{c} O{=}N{=}O \\ | \\ \boxed{O} \\ | \\ O{=}N{=}O \end{array}$$

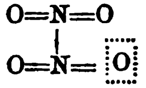
the oxygen atom in the dotted square is the first to go out, leaving the molecule $\left\{\begin{array}{l}\mathbf{N}O_2\\ \mathbf{N}O_2\end{array}\right.$ (nitric peroxide).



$$\begin{array}{c} O{=}N{=}O \\ | \\ O{=}N{=}O \end{array}$$

In both formulæ nitrogen acts the part of a *pentad* element.

$\mathbf{N}_2O_4$ would appear to contain an atom of oxygen less firmly united with the nitrogen atom; viz., the oxygen atom which has been placed within a dotted square—



$$\begin{array}{l} O{=}N{=}O \\ \quad\;\, | \\ O{=}N{=}\boxed{O} \end{array}$$

In the molecule of nitrous anhydride, $\mathbf{N}_2'''O_3$, nitrogen is a *triad* element, two of its bonds becoming latent, thus:—

$$O{=}N{-}O{-}N{=}O$$

It is evident from a glance at this formula that the oxygen atoms of $\mathbf{N}_2O_4$ must rearrange themselves, for we have again an atom of oxygen linking together the two nitrogen atoms, as in nitric anhydride.

In consequence of the unstable nature of free nitrous acid, it can be employed for purposes either of oxidation or reduction, as we shall see hereafter. Nitric peroxide breaks up according to the equation—

$$\mathbf{N}_2O_4 + \mathbf{O}H_2 = \mathbf{N}O_2Ho + \mathbf{N}OHo;$$

and nitrous acid according to the equation—

$$3\mathbf{N}OHo = \mathbf{N}O_2Ho + \mathbf{N}_2O_2 + \mathbf{O}H_2,$$

leaving as the ultimate products of decomposition of N_2O_4 only nitric acid and a colourless gas called nitric oxide, N_2O_2.

Experiment 67.—Introduce some copper turnings or clippings into a two-necked Woulfe's bottle, A, provided with a funnel and delivery-tube, B and C, Fig. 51. Nitric acid, diluted with about half its bulk of water, is then poured through the funnel into the bottle, which may be placed in a basin of cold water. The evolution of red fumes soon begins, and the air is gradually displaced by the gas. The red fumes within the bottle disappear (a sign that the air has been displaced), and at last the gas which comes off appears quite colourless. As soon as the gas which issues from the delivery-tube comes in contact with the air, it turns reddish brown. The fumes of this reddish brown gas are injurious when inhaled; the experiment must therefore be conducted in the open air or in a closet with sliding windows, and in a good draught. A glass cylinder is now filled with water rendered slightly alkaline by means of a few drops of sodic hydrate (in order to absorb any fumes of nitric acid that may be carried over), and inverted over the shelf of the pneumatic trough, and the gas collected in the usual manner by the displacement of the water in the cylinder. A perfectly colourless gas is thus obtained. The cylinder, when full, is closed under water by means of a glass plate, and then removed with its gaseous contents. On introducing several folds of litmus-paper moistened with water that is rendered slightly alkaline by means of a few drops of sodic hydrate, the gas turns instantaneously reddish brown at the mouth of the cylinder, where it comes in contact with the air. The blue litmus is seen to turn red as rapidly as the ruddy fumes form. When the cylinder has been filled half way down with these fumes, the glass plate is replaced and the lower part of the folds of litmus-paper is seen to remain blue in the colourless portion of the gas, whilst the upper part turns intensely red.

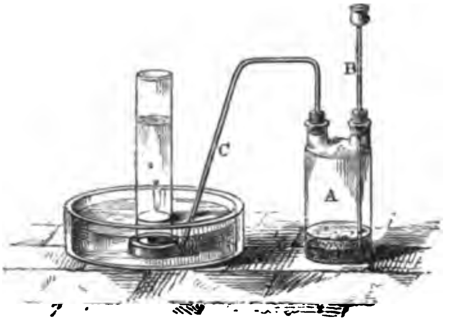


FIG. 51.

This experiment proves that the colourless gas obtained by the action of copper upon nitric acid is not an acid body, and that by mere contact with air it is converted into reddish-brown acid fumes, which are absorbed by water or by sodic hydrate. Since the oxygen and moisture of the air convert the colourless gas into an acid with which we have already become acquainted (viz., into nitrous acid), it is reasonable to suppose that the colourless gas is likewise an oxide of nitrogen, containing, however, less oxygen than nitrous acid: and since it does not react acid, it can only be one of the two remaining oxides, *i.e.*, it must be either N_2O_2 or ON_2. Now quantitative experiments have shown that the gas is composed of two atoms of nitrogen and two atoms of oxygen. It is written symbolically and graphically—

$$\left\{\begin{matrix} NO \\ NO \end{matrix}\right. \qquad \begin{matrix} N{=}O \\ | \\ N{=}O \end{matrix}$$

an atom of nitrogen being linked to another atom of nitrogen, leaving two more bonds free in each, which are satisfied by an atom of dyad oxygen.

The reaction* which took place when copper was treated with nitric acid must, therefore, be expressed by the following equation—

$$3Cu + 8\mathbf{N}O_2Ho = 3\begin{smallmatrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{smallmatrix}Cuo'' + \mathbf{N}_2O_2 + 4\mathbf{O}H_2,$$

and the deoxidation of a molecule of $\mathbf{N}_2O_5$, which we have previously seen accomplished, step by step, first to $\mathbf{N}_2O_4$, then to $\mathbf{N}_2O_3$, and lastly to $\mathbf{N}_2O_2$, is in this reaction attained at one leap.

Other metals, *e.g.*, lead and mercury, are acted upon by nitric acid in like manner, *i.e.*, they are converted into nitrates—

$$3Pb + 8\mathbf{N}O_2Ho = 3\begin{smallmatrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{smallmatrix}Pbo'' + \mathbf{N}_2O_2 + 4\mathbf{O}H_2.$$

$$3Hg + 8\mathbf{N}O_2Ho = 3\begin{smallmatrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{smallmatrix}Hgo'' + \mathbf{N}_2O_2 + 4\mathbf{O}H_2.$$

Others, again, deoxidize nitric acid to a less extent, such as tin and silver—

$$5Sn + 20\mathbf{N}O_2Ho = \underset{\text{Metastannic acid.}}{\mathbf{Sn}_5O_5Ho_{10}} + 5\mathbf{O}H_2 + \underset{\text{Nitric peroxide.}}{10\mathbf{N}_2O_4}.$$

$$4Ag + 6\mathbf{N}O_2Ho = 4\mathbf{N}O_2Ago + \underset{\text{Nitrous anhydride.}}{\mathbf{N}_2O_3} + 3\mathbf{O}H_2.$$

$$4Zn + 10\mathbf{N}O_2Ho = 4\begin{smallmatrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{smallmatrix}Zno'' + \underset{\text{Nitrous oxide.}}{\mathbf{O}N_2} + 5\mathbf{O}H_2.$$

In this latter reaction, however, the colourless gas $\mathbf{O}N_2$, called nitrous oxide (also known as laughing gas), is never free from the higher oxides, $\mathbf{N}_2O_2$, $\mathbf{N}_2O_3$, $\mathbf{N}_2O_4$; and the reaction is not nearly so perfect as that which took place when copper acted upon nitric acid. We may sum up by saying, *that ruddy vapours result from the action of nitric acid upon metals.*

Nitric acid oxidizes likewise most of the metalloids with evolution of red fumes. Powdered charcoal, when treated with $\mathbf{N}O_2Ho$ at a high temperature, decomposes it entirely with formation of carbonic anhydride and nitrogen. Sulphur is gradually oxidized into sulphuric acid; metallic sulphides into sulphates. Phosphorus is oxidized into phosphoric acid. Dilute nitric acid (sp. gr. 1·20) should be employed, and small pieces of phosphorus only should be introduced into the hot acid at a time. By employing amorphous, or red phosphorus, the danger of an explosion is avoided. Iodine is oxidized by strong boiling nitric acid into iodic acid, according to the equation:—

---

* There is invariably some ammonia (NH_3) formed in this and other similar reactions, and it would appear, therefore, that water, under favourable circumstances, takes part in the change.

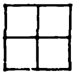
$$6\mathbf{N}O_2Ho + I_2 = 2\underset{\text{Iodic acid.}}{\left\{\begin{matrix}\mathbf{O}I\\ \mathbf{O}Ho\end{matrix}\right.} + 2\mathbf{O}H_2 + 2\mathbf{N}_2O_2 + \mathbf{N}_2O_4.$$

Wood, wool, horn, skin, silk, are stained yellow by dilute acid, and are converted by concentrated nitric acid into compounds of great practical importance, such as oxalic acid, gun-cotton, etc.

The five compounds which nitrogen is capable of forming with oxygen illustrate very well the law of constant combining proportions, according to weight and volume, as will be seen from the following table:—

		By volume.	By weight.
Nitrous oxide....	$\mathbf{O}N_2$	2 vols. of N, and 1 vol. of O.	$28 + 16 = 44.$
Nitric oxide	$\mathbf{N}_2O_2$	2 vols. of N, and 2 vols. of O	$28 + 32 = 60.$
Nitrous anhydride	$\mathbf{N}_2O_3$	2 vols. of N, and 3 vols. of O	$28 + 48 = 76.$
Nitric peroxide ..	$\mathbf{N}_2O_4$	2 vols. of N, and 4 vols. of O	$28 + 64 = 92.$
Nitric anhydride.	$\mathbf{N}_2O_5$	2 vols. of N, and 5 vols. of O	$28 + 80 = 108.$

We must content ourselves with merely referring in a tabular form to the molecular composition of these five bodies; remarking that nitric oxide and nitric peroxide show anomalous molecular volumes—

		Molecular weight.	Molecular volume.		Specific gravity referred to hydrogen.
Nitric anhydride.	$\mathbf{N}_2O_5$	108*	2 vols.*		54 criths.
Nitrous oxide....	$\mathbf{O}N_2$	44	2 vols.		22 „
Nitric oxide	$\mathbf{N}_2O_2$	60	4 vols.		15 „
Nitrous anhydride	$\mathbf{N}_2O_3$	76*	2 vols.*		38 „
Nitric peroxide..	$\mathbf{N}_2O_4$ 46 to 92		2 vols. at 0° C. to 4 vols. at 100° C.		23 to 46 criths.

All the preceding experiments have shown that we possess in

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[*] These molecular combinations have not been determined with absolute certainty, and the above figures represent merely their probable composition.

nitric acid (sometimes called *aqua fortis*) a powerful solvent for metals. This is owing either to the mobile nature of three out of the five oxygen atoms contained in each molecule; or to the slight resistance which the acid offers to the deoxidizing action of the elements, especially metals, whereby the nitric acid is partially or entirely deprived of its oxygen. Gold and platinum are not affected, *i.e.*, not oxidized, by nitric acid when in an unalloyed condition.

Aluminium strongly resists the action of nitric acid, even at a boiling heat.

Tin and antimony are converted into oxides, insoluble in nitric acid. Concentrated nitric acid does not act upon iron and tin at the ordinary temperature, though it dissolves them rapidly when diluted. When iron is immersed in concentrated nitric acid (sp. gr. 1·45), it remains unacted upon; and when subsequently placed in dilute acid, without first being wiped, it cannot be dissolved; it is said to assume the *passive* state. The cause of this peculiar action has not yet been satisfactorily explained.

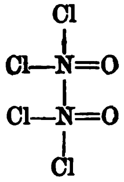
Comparatively few of the nitrates are commonly met with; the most important are—

Potassic nitrate (*nitre, saltpetre*)	$\mathbf{N}O_2Ko$.
Sodic nitrate (*cubic nitre*, or *Chili saltpetre*)	$\mathbf{N}O_2Nao$.
Baric nitrate	$\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Bao''$.
Strontic nitrate	$\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Sro''$.
Cobaltous nitrate	$\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Coo''$.
Plumbic nitrate	$\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Pbo''$.
Bismuthous nitrate	$\left.\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}\right]Bio'''$.
Argentic nitrate (*lunar caustic*)	$\mathbf{N}O_2Ago$.
Mercuric nitrate....................	$\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Hgo''$.

A mixture of six molecules of hydrochloric, and two molecules of nitric acid, is called *aqua regia* or *nitro-hydrochloric acid*—

$$2\mathbf{N}O_2Ho + 6HCl = \mathbf{N}_2O_2Cl_4 + 4\mathbf{O}H_2 + Cl_2.$$

The compound $\mathbf{N}_2O_2Cl_4$, chloronitric gas, graphic formula—



may be viewed as nitric peroxide, in which two atoms of dyad oxygen are replaced by four atoms of monad chlorine. $\mathbf{N}_2O_2Cl_4$ is of a still more unstable nature than the compound $\mathbf{N}_2O_4$. It forms a readily available source of chlorine, and is employed for dissolving gold and platinum; since chlorine acts in the nascent state on these metals, and forms with them soluble chlorides—

$$\mathbf{N}_2O_2Cl_4 + Pt = \mathbf{N}_2O_2 + \underset{\text{Platinic chloride.}}{\mathbf{Pt}^{iv}Cl_4}.$$

$$3\mathbf{N}_2O_2Cl_4 + 4Au = 3\mathbf{N}_2O_2 + \underset{\text{Auric chloride.}}{4\mathbf{Au}'''Cl_3}.$$

The $\mathbf{N}_2O_2$, on escaping into the air, gives rise to the well-known ruddy fumes; and aqua regia ought to be used only where there is a good draught to carry off these fumes.

Nitric oxide, $\mathbf{N}_2O_2$, which results from the action of nitric acid or aqua regia, escapes and partially recovers from the air the oxygen which the $\mathbf{N}O_2Ho$ gave up to the metals. Its tendency is to combine with two atoms of oxygen, and no more; and this oxygen it yields up again quite as readily to other bodies that have a stronger affinity for that element than either $\mathbf{N}_2O_3$ or $\mathbf{N}_2O_4$ possesses. Upon this remarkable property of nitric oxide is based one of the most beautiful and important processes, viz., the manufacture of oil of vitriol or sulphuric acid. We have seen that sulphur when burned in air combines with two atoms of oxygen to form sulphurous anhydride. Here, then, is a body that wants one more atom of oxygen in order to be converted into sulphuric anhydride, $\mathbf{S}O_3$: and in the $\mathbf{N}_2O_4$ we have a body that can readily part with one or two atoms of oxygen. Hence sulphuric anhydride must result from the reaction of these two bodies, according to the equations—

$$(1)\ \mathbf{S}O_2 + \mathbf{N}_2O_4 = \mathbf{S}O_3 + \mathbf{N}_2O_3.$$
$$(2)\ \mathbf{S}O_2 + \mathbf{N}_2O_3 = \mathbf{S}O_3 + \mathbf{N}_2O_2.$$

If we add to these two conditions, two others, viz., a well regulated supply of steam (to form sulphuric hydrate) and atmospheric air, or some other source of oxygen (to reoxidize the $\mathbf{N}_2O_2$ as fast as it is formed), the conversion of sulphurous into sulphuric acid becomes a continuous process. A peculiar white compound which is first formed is only a transitory product, and has little interest attached to it—

$$2\mathbf{S}O_2 + \mathbf{N}_2O_4 + O = \left\{\begin{array}{l}\mathbf{S}O_2(N^{v}O_2)\\ O\\ \mathbf{S}O_2(N^{v}O_2)\end{array}\right.$$

White crystalline compound.

which the water or steam, in its turn, decomposes—

$$\left\{\begin{array}{l}\mathbf{S}O_2(N^{v}O_2)\\ O\\ \mathbf{S}O_2(N^{v}O_2)\end{array}\right. + 2\mathbf{O}H_2 = 2\mathbf{S}O_2Ho_2 + \mathbf{N}_2O_3.$$

Nitrous anhydride, $\mathbf{N}_2O_3$, we have already seen cannot exist in the presence of water. It is at once broken up into nitric oxide and nitric acid—

$$3\mathbf{N}_2O_3 + \mathbf{O}H_2 = 2\mathbf{N}O_2Ho + 2\mathbf{N}_2O_2.$$

Nitric oxide, in the presence of air, is converted into nitric peroxide. The $\mathbf{N}O_2Ho$, and $\mathbf{N}_2O_4$ thus formed, can, in their turn, oxidize fresh quantities of $\mathbf{S}O_2$. By the proper supply of sulphurous anhydride, steam, air, and nitric peroxide, a continuous process of manufacture of this important substance—sulphuric acid—can be readily secured.

QUESTIONS AND EXERCISES.

1. Mention some natural saline compounds in which N occurs.
2. Explain the formation of saltpetre in tropical countries.
3. You have given to you Chili saltpetre and sulphuric acid. Describe how you would prepare nitric acid from these materials. Express the chemical change by an equation.
4. Calculate how much nitric acid ($\mathbf{N}O_2Ho$) by weight can be obtained from 20 grms. of nitre; and how much sulphuric acid ($\mathbf{S}O_2Ho_2$) by weight is required in order to have only dipotassic sulphate left in the retort.
5. Show why you write $\mathbf{N}O_2Ho$, and not NO_3H.
6. Give symbolic and graphic formulæ for nitric anhydride and nitric acid.
7. State how metallic nitrates are prepared. Give equations.
8. You have given to you a few iron nails, some pure tin foil, copper filings, and a little granulated zinc, with concentrated nitric acid and distilled water. State what chemical changes you can produce with these materials, and express the changes by equations.
9. Explain what takes place when cupric or bismuthous nitrate is heated in a retort.
10. What takes place when the vapour of $\mathbf{N}_2O_4$ is passed into a solution of baric hydrate? Express the changes by equations.
11. Give symbolic and graphic formulæ for nitric peroxide, nitrous anhydride, nitrous oxide, argentic nitrite.
12. Explain the action of concentrated nitric acid upon mercury and silver, sulphur, phosphorus, and iodine. Express the changes by equations.
13. Give a list of all the oxides of nitrogen, together with their atomic and volume weights.
14. What is the weight of ·10 litres of laughing gas?
15. Explain the terms *aqua fortis*, *aqua regia*, *cubic nitre*, *lunar caustic*.
16. Explain the action of aqua regia upon gold and platinum.
17. Show the important use of some of the nitrogen oxides in the manufacture of oil of vitriol.

18. Calculate the percentage composition of potassic nitrate.
19. How much argentic nitrate can be prepared from ten ounces of metallic silver?
20. What evidence have you to adduce that nitrogen occurs as a pentad, as a triad, and as a monad element?

CHAPTER XV.

AMMONIA.

FREE hydrogen and nitrogen possess very little affinity for one another, so that they cannot be united directly. A terhydride of nitrogen (three atoms of hydrogen and one atom of nitrogen), called *ammonia*, is known. This is for the most part derived from the nitrogen contained in nitrogenous organic substances, such as coal, hair, horn (whence its ordinary name of *spirit of hartshorn*), skin, sinews, etc. The greater part of the animal body (fat excepted) consists of organic substances rich in nitrogen; and they all yield, under certain conditions (dry distillation, putrefaction, etc.) the pungent gas called *ammonia*.

Experiment 68.—Rub together in a mortar a mixture of pulverized unslaked lime and caustic soda (called soda-lime) with some animal substance, such as glue, white of egg, horn shavings; then introduce the mixture into a test-tube, and apply heat. A pungent gas is given off, which turns red litmus-paper blue, and yields white fumes when a glass rod moistened with dilute hydrochloric acid is held in the gas.

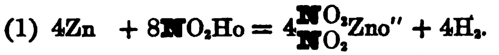
Experiment 69.—Treat a little zinc with dilute sulphuric acid; hydrogen gas is evolved—

$$Zn + \mathbf{S}O_2Ho_2 = \mathbf{S}O_2Zno'' + H_2.$$

Add now, drop by drop, dilute nitric acid. The evolution of gas ceases, but the zinc nevertheless disappears. The hydrogen combines with the elements of nitric acid to form water and ammonia, which latter immediately enters into combination with the acids:—

$$\begin{aligned}
&(1)\ 4H_2 + \mathbf{N}O_2Ho = \mathbf{N}H_3 + 3\mathbf{O}H_2.\\
&(2)\ \mathbf{N}H_3 + \mathbf{N}O_2Ho = \mathbf{N}O_2(NH_4O).\\
&\ 2\mathbf{N}H_3 + \mathbf{S}O_2Ho_2 = \mathbf{S}O_2(NH_4O)_2.
\end{aligned}$$

A similar reaction takes place when zinc is dissolved in moderately dilute nitric acid. Owing to a secondary reaction, hydrogen and nitrogen combine to form ammonia, and zincic and ammonic nitrate are left—



$$(1)\ 4Zn + 8\mathbf{N}O_2Ho = 4\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Zno'' + 4H_2.$$

$$\begin{aligned}
&(2)\ 4H_2 + \mathbf{N}O_2Ho = \mathbf{N}H_3 + 3\mathbf{O}H_2.\\
&(3)\ \mathbf{N}H_3 + \mathbf{N}O_2Ho = \mathbf{N}O_2(NH_4O).
\end{aligned}$$

Quantitative experiments have shown that ammonia gas consists of H_3 and N, and its composition is expressed by the formula $\mathbf{N}H_3$.

The action of nitric acid upon zinc is invariably accompanied by the formation of lower oxides of nitrogen, $\mathbf{O}N_2$, $\mathbf{N}_2O_3$, etc., which offer little resistance to the action of the hydrogen, and yield under favourable circumstances nitrogen and water. Both nitrogen and hydrogen, when in the nascent state, *i.e.*, at the very moment[*] of their liberation, combine and form ammonia, $\mathbf{N}H_3$. The solution contains a considerable amount of ammonic nitrate, which may be proved by heating some of it with a little soda-lime.

Experiment 70.—Heat some ammonic nitrate in a Florence flask, provided with a delivery-tube, or in a small retort (Fig. 52). The salt melts, boils, and gradually breaks up into nitrous oxide (or laughing gas), $\mathbf{O}N_2$, and steam. The gas may be collected over water.

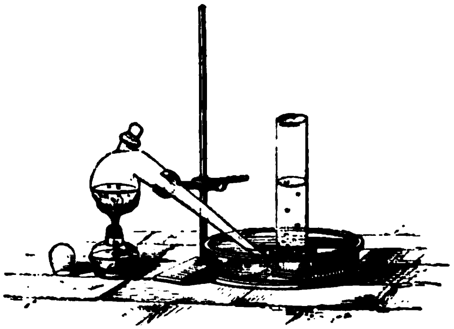


Fig 52.

The decomposition of ammonic nitrate takes place, according to the equation:—

$$\mathbf{N}O_2(NH_4O) = \mathbf{O}N_2 + 2\mathbf{O}H_2.$$

Nitrous oxide is a colourless gas, with a slight smell and a sweetish taste. Its specific gravity, compared with air, is 1·527; its volume weight (H = 1) is 22. One litre of $\mathbf{O}N_2$ weighs 22 × ·0896 grm. = 1·9712 grm. Nitrous oxide, when mixed with air, undergoes no change. Water absorbs it to a certain extent (1·3 of its volume at 0° C.). A glowing piece of charcoal, when introduced into the gas, burns almost as brilliantly as we saw carbon burn in oxygen (comp. Exp. 22). A glowing splinter of wood bursts into flame, and burns brilliantly in the gas. Atmospheric air, we know, sustains respiration. Certain animals are able to breathe nitrous oxide (which we may view as an air considerably richer in oxygen — 36·4 P.C.) with impunity for several hours. When inhaled by man, it produces a characteristic kind of exhilarating intoxication, which is sometimes accompanied by immoderate laughter; hence its name *laughing gas*. Pure gas only should be employed for purposes of inhalation. Nitrous oxide has of late been recommended as an

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[*] The elements may be supposed to exist for a moment in the uncombined state.

anæsthetic, or agent for suspending the mental and sensorial functions during dental and surgical operations.

Ammonic nitrite heated in like manner yields nitrogen and water, according to the equation—

$$\mathbf{N}'''O(NH_4O) = N_2 + 2\mathbf{O}H_2.$$

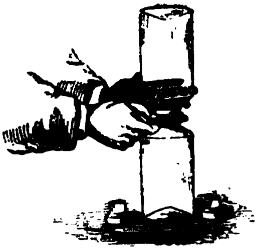


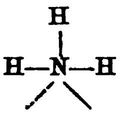
Fig. 53.

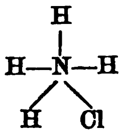
Experiment 71.—Fill a wide-mouthed bottle or cylinder with ammonia gas, by rinsing it out with a few drops of strong solution of ammonia (the *liquor ammoniæ* of the shops); cover it with a glass plate. Another cylinder or bottle is filled with hydrochloric acid gas. The two bottles or cylinders are then placed together (as seen in Fig. 53), and the glass plates withdrawn, so that the mouth of the inverted vessel containing the hydrochloric acid gas rests almost air-tight on the mouth of the lower vessel. Both gases are seen to mix, and to combine, producing clouds of white fumes.

These clouds are deposited on the sides of the glass vessels as a white salt, called ammonic chloride (*sal-ammoniac*), a compound of the ammonia and hydrochloric acid gas—

$$\mathbf{N}'''H_3 + HCl = \mathbf{N}^{v}H_4Cl.$$

The nitrogen atom in $\mathbf{N}H_3$ is combined only with three atoms of hydrogen, and is therefore triadic; but it is also clear from the avidity with which $\mathbf{N}H_3$ combines with HCl, that two more affinities remain *latent*, one of which can become satisfied by hydrogen, the other by chlorine, thus:—





Experiment 72.—Heat gently in a test-tube a concentrated solution of ammonic chloride in water, with sodic or potassic hydrate. Ammonia gas is evolved, according to the equation—

$$\mathbf{N}H_4Cl + NaHo = \mathbf{N}H_3 + NaCl + \mathbf{O}H_2.$$

and is readily recognised, 1st. by its characteristic pungent odour; 2nd. by its action upon red litmus-paper or turmeric-paper (changed from red to blue, and from yellow to brown); and 3rd. by the white clouds which it produces when a glass rod, moistened with dilute hydrochloric, sulphuric, or nitric acid is held at the mouth of the test-tube.

Ammonia forms with these acids the respective salts—

$\mathbf{N}H_3 + HCl = \mathbf{N}H_4Cl$ (Ammonic chloride).
$2\mathbf{N}H_3 + \mathbf{S}O_2Ho_2 = \mathbf{S}O_2(NH_4O)_2$ (Ammonic sulphate).
$\mathbf{N}H_3 + \mathbf{N}O_2Ho = \mathbf{N}O_2(\mathbf{N}H_4O)$ (Ammonic nitrate).

The compound NH_4 appears to be capable of existing only as an amalgam.* It is obtained by mixing sodium-amalgam ($Hg_n\ Na_m$) with a concentrated solution of ammonic chloride—

$$Hg_nNa_m + {}_m\mathbf{N}H_4Cl = Hg_n(NH_4)_m + {}_mNaCl.$$

Na exerts its well known affinity for Cl, forming with it sodic chloride; $2Hg_n$ no change, $(NH_4)_m$, breaking up very rapidly into $2nHg$, $2m\mathbf{N}H_3$, and mH_2, which is evolved. On account of its salts possessing a marked similarity with potassic and sodic salts, the existence of a hypothetical metal ammonium, NH_4, has been entertained by chemists. Ammonium is affected like the alkali metals, potassium and sodium. Its haloid salts, $\mathbf{N}H_4Cl$, $\mathbf{N}H_4I$, $\mathbf{N}H_4Br$, which are well defined salts, can therefore also be viewed as derived from

$$\begin{aligned}\mathbf{N}H_3 + H + Cl &= \mathbf{N}H_4Cl.\\ \mathbf{N}H_3 + H + I &= \mathbf{N}H_4\,I \text{ (Ammonic iodide)}.\\ \mathbf{N}H_3 + H + Br &= \mathbf{N}H_4Br \text{ (Ammonic bromide)}.\end{aligned}$$

by assuming that the atom hydrogen attacks the molecule $\mathbf{N}H_3$ first, forming with it NH_4, or the hypothetical metal called—in accordance with the terminology adopted by chemists—*Ammonium*. Since this metal combines with one atom of chlorine, it must be viewed as a monad, like potassium or sodium; and as it consists of one atom of nitrogen and four atoms of hydrogen, and yet acts the part of an element, it is called a compound radical. It is usually written Am, instead of NH_4, forming ammonoxyl, Amo, analogous to the radicals Ho, Ko, etc.

Ammonic hydrate formed, according to the equation—

$$\mathbf{N}H_3 + \mathbf{O}H_2 = \mathbf{N}H_4Ho,$$

appears likewise to have only a hypothetical existence, as no chemical combination seems to take place between the water and the ammonia; for the gas gradually escapes on exposing the solution to the air, and no definite compound of ammonia and water has been observed. The escape of the gas from the solution is marked by the production of intense cold: *i.e.*, much heat becomes latent, when ammonia is converted from the liquid to the gaseous state. This property has found a practical application for refrigerating purposes, and for producing ice artificially.

Ammonic chloride, sulphate, or nitrate, are best obtained by the action of the respective acids upon the ammonic hydrate:—

$$\begin{aligned}AmHo + HCl &= AmCl + \mathbf{O}H_2.\\ 2AmHo + \mathbf{S}O_2Ho_2 &= \mathbf{S}O_2Amo_2 + 2\mathbf{O}H_2.\\ AmHo + \mathbf{N}O_2Ho &= \mathbf{N}O_2Amo + \mathbf{O}H_2.\end{aligned}$$

Experiment 73.—Heat a little sal-ammoniac in an iron spoon, or on platinum foil. White fumes are given off. When heated in a test-tube, the fumes condense in the upper or colder part of the tube; the salt sublimes unchanged.

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* Compounds of the metal mercury with other metals, are called *amalgams*.

Most salts of ammonium *volatilize* upon ignition.

This property renders ammonium salts of great value in chemical analysis.

A solution of ammonia gas in water, is indispensable in the laboratory. It is therefore important to study its preparation and properties.

Experiment 74.—Ammonia gas is very soluble in water. This may be shown by heating a little strong ammonia in a small retort (Fig. 54), and filling a dry flask with the gas by downward displacement, and when full, plunging the mouth of the flask rapidly under water. The latter rushes in most eagerly. The liquid which is left in the flask reacts alkaline. Water absorbs about 700 times its bulk of the gas.

A concentrated solution of ammonia is obtained by distilling in a flask a mixture of sal-ammoniac and calcic hydrate.

The gas is made to pass through a wash-bottle, containing a little water, and from thence through one or more Woulfe's bottles, filled about three-fourths with water (as shown in Fig. 41). The delivery-tubes must reach nearly to the bottom, as aqueous ammonia is lighter than water.

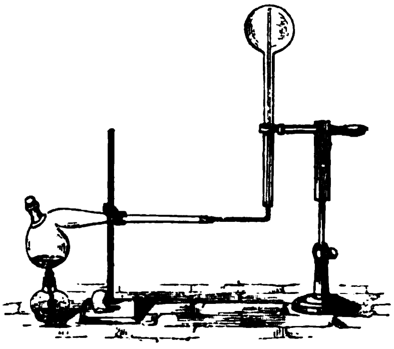

FIG. 54.

Ammonia gas is obtained dry by passing it over freshly-burnt lime.* It may be collected by displacement (imperfectly), or over mercury.

Its composition by volume and by weight has been carefully determined.

The volumetrical composition of ammonia cannot, however, be demonstrated so readily, as, for instance, that of steam or hydrochloric acid gas. Ammonia is decomposed by bringing it into contact with chlorine; and for every three volumes of chlorine so employed, one volume of nitrogen is left. The hydrochloric acid, resulting from the combination of hydrogen and chlorine, combines with the excess of ammonia, and forms the solid salt, NH_4Cl.

By passing electric sparks for some time through dry ammonia gas, placed in a eudiometer-tube over mercury, the gas is slowly decomposed into its component elements, hydrogen and nitrogen. The gas volume is seen to increase gradually, till the original volume has been doubled. The four volumes of mixed gases were found on analysis to consist of three volumes of hydrogen and one volume of nitrogen; and one volume of ammonia gas is derived from $1\frac{1}{2}$ volumes of hydrogen and $\frac{1}{2}$ of nitrogen, weighing respectively ·1038 and ·4856, total = ·5894 (sp. gr. of $\mathbf{H}$ = ·0693, and of $\mathbf{N}$ = ·9712, when compared with air).

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* Calcic chloride cannot be used, because it absorbs a considerable quantity of the gas; nor oil of vitriol, because ammonia combines with the acid with explosive violence.

Direct estimation of the specific gravity of ammonia gas (compared with air) gave the number ·597, from which the above differs but little.

The percentage composition is readily found by rule of three calculation, viz.:—

Hydrogen	17·61
Nitrogen	82·39

The molecular weight of $\mathbf{N}H_3$ is 17. The specific gravity of ammonia gas compared with hydrogen, is therefore 8·5, and one litre of ammonia gas weighs $\frac{17}{2} = 8{\cdot}5 \times {\cdot}0896$ grm. = ·7616 grm.

A few compounds of ammonia briefly claim our attention, as they constitute some of our most important reagents.

Experiment 75.—Measure out two equal portions of a solution of ammonia or ammonic hydrate, also called simply ammonia. Pass through one portion a brisk current of sulphuretted hydrogen gas, as long as the gas continues to be absorbed. (The apparatus described for the preparation of chlorine water answers admirably.) Then add the second portion to it, and a solution of ammonic sulphide, $\mathbf{S}Am_2$, is obtained.

By completely saturating a solution of ammonia with sulphuretted hydrogen, we obtain a solution of hydric ammonic sulphide, AmHs, in which the compound radical hydrosulphyl, Hs, has taken the place of the hydroxyl, thus:—

$$AmHo + \mathbf{S}H_2 = AmHs + \mathbf{O}H_2.$$

On then adding AmHo to this solution, ammonic sulphide is obtained, thus:—

$$AmHs + AmHo = \mathbf{S}Am_2 + \mathbf{O}H_2.$$

Experiment 76.—Fill a cylinder with dry carbonic anhydride gas, and another cylinder of double the size with dry ammonia gas. On bringing the mouths of the two cylinders towards each other, the two gases rush together, and form the compound $_2NH_3,CO_2$. This body attracts moisture rapidly, and dissolves to a salt having the composition $\mathbf{C}OAmo_2$, ammonic carbonate.

Experiment 77.—Pass a current of $\mathbf{C}O_2$ through a concentrated solution of ammonia as long as any gas is absorbed. On setting the solution aside for crystallisation beautiful colourless rhombic prisms are obtained, which have the composition $\mathbf{C}OHoAmo$ (hydric ammonic carbonate).

Notice the smell of the crystals.

Solutions of both these ammonium compounds are employed in the laboratory.

QUESTIONS AND EXERCISES.

1. Which are the chief sources whence ammonia and its compounds are derived?
2. You have given to you some coal and soda-lime. Show how you would prepare NH_3 from these materials.
3. Explain the formation of ammonia by the aid of dilute sulphuric acid, metallic zinc, and dilute nitric acid. Express the changes by equations.
4. How would you prepare, 1st, nitrogen; 2nd, nitrous oxide gas?
5. What are the properties of nitrous oxide?
6. You have given to you 25 grms. of pure ammonic nitrate. How much laughing-gas, by weight and by volume, can you prepare from it?
7. Write out the symbolic and graphic formulæ for ammonia, ammonic bromide, carbonate, and hydric ammonic sulphide.
8. Explain the terms *amalgam*, *nascent state*, *sal-ammoniac*, *spirit of hartshorn*.
9. Describe the formation of ammonium-amalgam, and give reasons why the group of elements, NH_4, is considered to be a metal.
10. Why are NH_4 and AmHo considered hypothetical compounds?
11. How would you show experimentally that most ammonium compounds can be *volatilized* and *sublimed*?
12. What space will 5·324 grms. of ammonia gas occupy at 15° C., and 745 mm. barometric pressure?
13. How are neutral ammonic sulphide and hydric ammonic carbonate prepared?
14. How would you prepare dry ammonia gas?
15. How is a concentrated solution of ammonia in water (*liquor ammoniæ*) prepared?

CHAPTER XVI.

THE OXIDES OF PHOSPHORUS AND ARSENIC.

PHOSPHORUS, when pure, is a wax-like, faintly yellow, semi-opaque, solid body. It is generally sold in the form of sticks. It melts readily at 44° C., and becomes then of a yellowish syrupy consistency. It can be distilled, its boiling-point being 288° C. Phosphorus volatilizes, however, far below its boiling-point. Its great inflammability constitutes its most characteristic property. Friction may set it on fire. Dry phosphorus when exposed to the air combines slowly with oxygen, and its temperature is often raised so considerably by this slow combustion that it melts and inflames spontaneously, especially in warm weather. It has therefore to be preserved in cold water, in which it is quite insoluble.

We have already seen (comp. Exp. 21) that phosphoric anhydride results from the combination of phosphorus with oxygen.

Experiment 78.—Small quantities of this body may be prepared by burning some phosphorus placed in a little porcelain capsule under a good-sized bell-jar resting on a plate as seen in Fig. 55. The phosphorus should be well dried, and the bell-jar wiped quite dry. A snow-white powder is deposited on the sides of the jar, which may be scraped together with a glass spatula, and kept in a well-stoppered bottle. The white powder has a great affinity for water, with which it combines with a hissing noise. On account of this great attraction for water it is often used as a *dehydrating agent.*

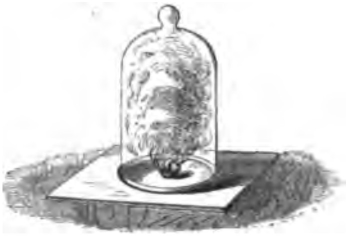
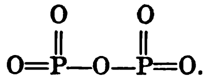


FIG. 55.

Analysis has proved that this white body consists of 2 atoms of pentad phosphorus, and 5 atoms of oxygen; hence we write its symbolic formula $\mathbf{P}_2{}^{v}O_5$, and its graphic formula:—



$$\mathrm{O{=}\overset{\overset{\textstyle O}{\|}}{P}{-}O{-}\overset{\overset{\textstyle O}{\|}}{P}{=}O.}$$

Phosphoric anhydride combines with water to form the hydrated acid, thus:—

$$\mathbf{P}_2O_5 + 3\mathbf{O}H_2 = 2\mathbf{P}OHo_3.$$

Phosphoric anhydride. Phosphoric acid.

There exist three phosphoric hydrates, differing markedly in their properties when in combination with bases.

If a solution of phosphoric acid be evaporated in a platinum vessel till it has acquired a syrupy consistency, hard transparent crystals of trihydric acid are obtained. At a higher temperature (160° to 210°) water is given off slowly, and the tetrahydric acid is left, called pyrophosphoric acid (from πῦρ, fire), on account of its being produced from the trihydric acid by the application of heat according to the equation:—

$$2\mathbf{P}OHo_3 = \mathbf{P}_2O_3Ho_4 + \mathbf{O}H_2.$$

Pyrophosphoric acid.

At a red heat the pyrophosphoric acid loses a molecule of water, leaving two molecules of the monohydric or metaphosphoric acid, thus:—

$$\mathbf{P}_2O_3Ho_4 = 2\mathbf{P}O_2Ho + \mathbf{O}H_2.$$

Metaphosphoric acid.

The trihydric acid is also called *orthophosphoric acid* (from ὀρθὸς, right), and *common* phosphoric acid, because it occurs in the phosphates most commonly employed in the arts. It contains 3 atoms of the compound-radical hydroxyl, and is capable of forming with the monad radicals potassoxyl or sodoxyl, by the partial or total displacement of the hydroxyl in the acid, three different kinds of salts called orthophosphates, viz.:—

$\mathbf{P}ONao_3$, Trisodic phosphate.
$\mathbf{P}OHoNao_2$, Common, or hydric disodic phosphate.
$\mathbf{P}OHo_2Nao$, Dihydric sodic phosphate.

When phosphoric hydrate, or phosphoric acid, is neutralized with sodic hydrate and then evaporated to crystallisation, the second salt is obtained in large transparent, oblique rhombic prisms, which effloresce rapidly in the air. These crystals contain water of crystallisation, and the salt has the composition $\mathbf{P}OHoNao_2 + 12Aq$. (Aq., abbreviation for *aqua*, water, standing for *water of crystallisation*). A solution of this phosphate gives, with a solution of argentic nitrate, a *yellow* precipitate of *triargentic phosphate*,—Ago (argentoxyl) replacing the hydroxyl and sodoxyl, thus:—

$$\mathbf{P}OHoNao_2 + 3\mathbf{N}O_2Ago = \mathbf{P}OAgo_3 + 2\mathbf{N}O_2Nao + \mathbf{N}O_2Ho,$$

the liquid being acid.

Experiment 79.—Heat gently a small quantity of the ordinary hydric disodic phosphate in a porcelain dish on a water-bath (Fig. 56). The salt fuses first in its water of crystallisation, then swells up, and gives off puffs of steam, the water escaping from underneath the crust of the solidified salt. Cease heating when no more water escapes, and the liquid salt becomes once more solid. On dissolving a small portion of the white mass in water, and adding a solution of argentic nitrate, the same yellow precipitate will be obtained which the salt gave before being heated. It has not been changed beyond losing its 12 molecules of water of crystallisation. On dissolving in hot water, and allowing to crystallise, the original rhombic prisms are obtained once more.

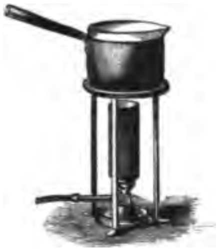


Fig. 56.

Heat some of the dry salt in an iron spoon, or, better, in a platinum vessel, to a strong red heat over a gas flame. Water is again expelled—the water which formed part of the salt, so called water of constitution—and on dissolving a little of the white saline residue in water, and adding a solution of argentic nitrate, a white precipitate is now obtained, and the solution is neutral, an indication that the salt has undergone a change. On dissolving some of the ignited mass in hot water, and setting it aside to crystallise, the solution no longer deposits crystals of the original salt, but of a salt which, on analysis, is found to consist of $\mathbf{P}_2O_3Nao_4$ (sodic pyrophosphate).

Its formation is expressed by the equation:—

$$2\mathbf{P}OHoNao_2 = \mathbf{P}_2O_3Nao_4 + \mathbf{O}H_2.$$

This salt contains no longer trihydric, but tetrahydric phosphoric acid, $\mathbf{P}_2O_3Ho_4$, called pyrophosphoric acid.

Experiment 80.—We are acquainted with a characteristic salt of ordinary or orthophosphoric acid, called *microcosmic salt*, or hydric ammonic sodic phosphate ($\mathbf{P}O\ Ho\ Amo\ Nao + 8\ Aq$). This salt may be readily prepared by dissolving 6 to 7 parts of the common sodic phosphate of commerce, and 1 part of ammonic chloride in 2 parts of boiling water, and allowing the liquid to crystallise in a cool place. On heating the salt in the same manner as was done in the previous experiment, a clear transparent mass is left, which, if slowly cooled becomes crystalline; it now deliquesces in air, and dissolves very readily in water. The aqueous solution when almost neutral, gives with argentic nitrate a white precipitate. The supernatant liquid is neutral. Water of crystallisation and ammonia are given off, and the salt, $\mathbf{P}\mathrm{O_2Nao}$ (sodic metaphosphate), is left, which contains no longer trihydric, but monohydric phosphoric acid.

The change may be expressed by the equation:—

$$\mathbf{P}\mathrm{OHoAmoNao} = \mathbf{P}\mathrm{O_2Nao} + \mathbf{N}\mathrm{H_3} + \mathbf{O}\mathrm{H_2}.$$

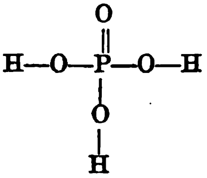
Sodic
Metaphosphate.

We have thus become acquainted with three modifications of phosphoric acid, not to speak of other forms, viz.:—

1. Common or orthophosphoric acid, $\mathbf{P}\mathrm{OHo_3}$ (trihydric or tribasic).
2. Pyrophosphoric acid, $\mathbf{P}_2\mathrm{O_3Ho_4}$ (tetrahydric or tetrabasic).
3. Metaphosphoric acid, $\mathbf{P}\mathrm{O_2Ho}$ (monohydric or monobasic).

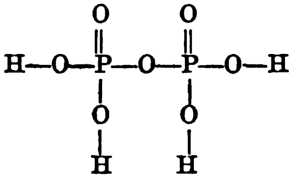
Pentad phosphorus being invariably the grouping element, these acids are written symbolically and graphically, thus:—

$\mathbf{P}\mathrm{OHo_3}$



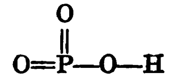
$$\begin{array}{ccccccccc} & & & & \mathrm{O} & & & & \\ & & & & \| & & & & \\ \mathrm{H} & - & \mathrm{O} & - & \mathrm{P} & - & \mathrm{O} & - & \mathrm{H} \\ & & & & | & & & & \\ & & & & \mathrm{O} & & & & \\ & & & & | & & & & \\ & & & & \mathrm{H} & & & & \end{array}$$

$\mathbf{P}_2\mathrm{O_3Ho_4}$



$$\begin{array}{ccccccccccccc} & & & & \mathrm{O} & & & & \mathrm{O} & & & & \\ & & & & \| & & & & \| & & & & \\ \mathrm{H} & - & \mathrm{O} & - & \mathrm{P} & - & \mathrm{O} & - & \mathrm{P} & - & \mathrm{O} & - & \mathrm{H} \\ & & & & | & & & & | & & & & \\ & & & & \mathrm{O} & & & & \mathrm{O} & & & & \\ & & & & | & & & & | & & & & \\ & & & & \mathrm{H} & & & & \mathrm{H} & & & & \end{array}$$

$\mathbf{P}\mathrm{O_2Ho}$



$$\begin{array}{ccccccc} & & \mathrm{O} & & & & \\ & & \| & & & & \\ \mathrm{O} & = & \mathrm{P} & - & \mathrm{O} & - & \mathrm{H} \end{array}$$

A lower oxide, formed by slow and imperfect oxidation of phosphorus (as when it is exposed to dry air at the ordinary temperature), viz., *phosphorous anhydride*, consisting of 2 atoms of phosphorus and 3 atoms of oxygen, is obtained in the form of a white powder possessing the odour of garlic. Its symbolic formula is $\mathbf{P}'''_2\mathrm{O}_3$, its graphic formula:—

$$\mathrm{O{=}P{-}O{-}P{=}O},$$

the P being in the triad condition, with two bonds left dormant in each atom. Phosphorous anhydride is of interest in so far only as it acts as a powerful reducing agent; *i.e.*, owing to its latent bonds it can deprive other oxides of part of their oxygen. Of the many reactions illustrative of this property, we will only cite the action of $\mathbf{P}_2O_3$ on silver salts, thus:—

$$2\mathbf{O}Ag_2 + \mathbf{P}_2O_3 = 2Ag_2 + \mathbf{P}_2O_5.$$

Phosphorus is capable of combining also with hydrogen.

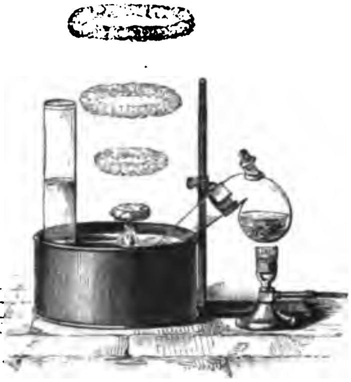


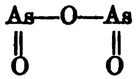
FIG. 57.

Experiment 81.—Introduce into a small retort (Fig. 57) some concentrated solution of potassic or sodic hydrate, and a few small pieces of phosphorus. On heating, a gaseous body is evolved, which ignites spontaneously, as soon as it issues from the water of the pneumatic trough. Each gas bubble rises through the air with a peculiar circular wreath of white smoke, which enlarges as it ascends in the air.

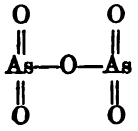
Phosphorus alone does not decompose water. It requires the powerful base potash or soda to induce it to form with the oxygen of the water an oxy-acid, and with the hydrogen an inflammable gas, called *phosphoretted hydrogen*, thus:—

$$3\mathbf{O}KH + P_4 + 3\mathbf{O}H_2 = \underset{\text{Potassic hypophosphite.}}{3\mathbf{P}OH_2Ko} + \underset{\text{Phosphoretted hydrogen.}}{\mathbf{P}H_3}.$$

Bodies which appertain to the metals rather than to the nonmetals, such as arsenic (As), antimony (Sb), bismuth (Bi), but which form compounds analogous with the compounds of phosphorus, must be briefly glanced at here. These elements are like phosphorus, of a pentad nature. Arsenic, moreover, occurs in nature, closely associated with phosphorus. This close resemblance extends also to the oxides of arsenic and their salts, the *arsenites* and *arseniates*. Two oxides deserve our attention, *arsenious*, $\mathbf{As}'''_2O_3$, and *arsenic anhydride*, $\mathbf{As}^{v}_2O_5$, written graphically:—



$$\begin{array}{ccc} As & — O — & As \\ \| & & \| \\ O & & O \end{array}$$



$$\begin{array}{ccc} O & & O \\ \| & & \| \\ As & — O — & As \\ \| & & \| \\ O & & O \end{array}$$

In the lower oxide each atom of arsenic has two bonds left unsatisfied; and very interesting reactions, based upon the deoxidation of various higher oxides, by means of arsenious anhydride, result from this property, which will be described hereafter.

Arsenic is sometimes found native, but more frequently in combination with metals, such as iron, nickel, cobalt, etc. When arsenic is combined with metals, it forms with them *arsenides*, from which the arsenic can be removed by roasting (in a reverberatory furnace), in the form of a volatile oxide, which is condensed in brick flues, and purified by sublimation.

Experiment 82.—Heat a small quantity of some finely powdered arsenide, such as arsenical pyrites, or *mispickel*, in a piece of hard glass tube (combustion-tube), holding the tube in a slightly inclined position, so as to cause a current of air to pass over the ignited powder. The sulphur and arsenic combine with oxygen to form volatile compounds, viz., sulphurous anhydride, $\mathbf{S}O_2$, and arsenious anhydride, $\mathbf{As}_2O_3$, leaving the iron as oxide. The $\mathbf{As}_2O_3$ condenses in the cold part of the tube, and $\mathbf{S}O_2$ passes off.

The change takes place according to the equation:—

$$As_4 + 3O_2 = 2\mathbf{As}_2O_3.$$

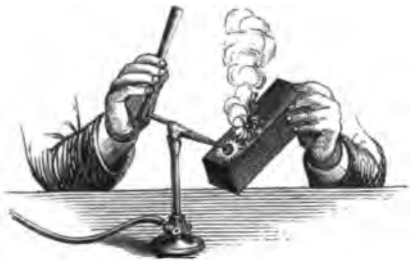


FIG. 58.

Experiment 83.—By heating a little of the arsenious anhydride or white arsenic so obtained on charcoal, before the blowpipe (Fig. 58), a strong garlic odour becomes at once perceptible, and white fumes ascend into the air, which are highly poisonous. The experiment should therefore be made with a very small quantity of the substance only, and in a place with a good draught. The charcoal deprives the arsenious anhydride of its oxygen, forming $\mathbf{C}O_2$ and As. The metallic arsenic being readily volatilized, on passing through the outer or oxidizing cone of the blowpipe flame, is partially reconverted into oxide, thus:—

$$(1)\ 2\mathbf{As}_2O_3 + 3C = As_4 + 3\mathbf{C}O_2.$$
$$(2)\ As_4 + 3O_2 = 2\mathbf{As}_2O_3.$$

Arsenious differs from phosphorous anhydride by possessing but little affinity for oxygen. It requires in fact powerful oxidizing agents, such as nitric acid, to convert it into arsenic acid, $\mathbf{As}OHo_3$.

Experiment 84.—Dissolve a little powdered white arsenic in a small flask, in hot hydrochloric acid (as it is but slightly soluble in water), and oxidize by means of concentrated nitric acid, as long as ruddy fumes of $\mathbf{N}_2O_3$ are evolved. The liquid is then cautiously evaporated to complete dryness, and a little water added to a small portion. The mass dissolves completely, showing a strongly acid reaction to test-paper.

The reaction takes place according to the equation:—

$$\mathbf{As}_2O_3 + 2\mathbf{N}O_2Ho + 2\mathbf{O}H_2 = \underset{\text{Arsenic acid.}}{2\mathbf{As}OHo_3} + \mathbf{N}_2O_3.$$

Arsenic anhydride has, like phosphoric anhydride, a great attraction for water. It absorbs moisture from the air, and gradually deliquesces. The solution contains trihydric or tribasic arsenic acid, precisely analogous to orthophosphoric acid, forming salts which are identical in shape (isomorphous) with the corresponding phosphates. A sodic arseniate, $\mathbf{As}OHoNao_2 + 12$ aq., is obtained, when arsenic acid is neutralized with sodic hydrate or sodic carbonate, which cannot be distinguished in appearance from the common sodic phosphate.

Like phosphoric acid it can form three different kinds of salts, viz. :—

$\mathbf{As}ONao_3$,	Trisodic arseniate,
$\mathbf{As}OHoNao_2$,	Common arseniate, or hydric disodic arseniate,
$\mathbf{As}OHo_2Nao$,	Dihydric sodic arseniate,

and is capable of retaining one or two parts of unreplaced hydroxyl, or of replacing two parts of hydroxyl by Mgo'', or some other oxyl-radical of a dyad metal, as in $\mathbf{As}OAmoMgo''$, ammonic magnesic arseniate. Salts are also derived from the acid in which the analogy between arsenic and phosphoric acid is still further borne out. We know salts containing—

$\mathbf{As}O_2Ho$,	and	$\mathbf{As}_2O_3Ho_4$,
Metarsenic acid.		Pyrarsenic acid.

Corresponding to—

$\mathbf{P}O_2Ho$,	and	$\mathbf{P}_2O_3Ho_4$.
Metaphosphoric acid.		Pyrophosphoric acid.

Arsenious acid forms likewise a definite series of salts, called arsenites, closely analogous to phosphites, of which the alkaline arsenites possess again the greatest interest. The power of forming salts with different bases which this acid possesses is, however, not so well defined as that of arsenic acid.

The compounds which arsenic and antimony are capable of forming with hydrogen, analogous to phosphoretted hydrogen, $\mathbf{P}H_3$, viz., arsenietted hydrogen, $\mathbf{As}H_3$, and antimonietted hydrogen, $\mathbf{Sb}H_3$, will be described below, under the respective metals.

QUESTIONS AND EXERCISES.

1. Describe the most important properties of phosphorus.
2. How would you prepare small quantities of phosphoric anhydride?
3. Explain how orthophosphoric, pyrophosphoric, and metaphosphoric acid are obtained. Give equations.
4. You have given to you a solution of orthophosphoric acid, and a solution of potassic hydrate. State what salts you can form with these materials?
5. Give symbolic and graphic formulæ for common sodic phosphate, magnesic pyrophosphate, sodic metaphosphate, and phosphorous anhydride.
6. How would you distinguish between a soluble orthophosphate and pyrophosphate?
7. Explain the terms, *dehydrating agent*, *water of crystallisation*, *ortho-* and *pyrophosphoric acid*, *microcosmic salt*, *arsenide*.
8. Describe the changes which microcosmic salt and the common hydric disodic phosphate undergo, when exposed to a gradually increasing heat. Give equations.

9. How is phosphorous anhydride prepared, and what is its most characteristic property?
10. Trace the analogy which exists between phosphorus and arsenic compounds.
11. What changes do metallic arsenides undergo when heated in a tube of hard glass, open at both ends? Give equations.
12. How is white arsenic affected when heated on charcoal before the blow-pipe flame? Give equations.
13. In what respect does phosphorous anhydride differ from arsenious anhydride?
14. What is the action of nitric acid upon arsenious anhydride? Give an equation.
15. Write out the symbolic formulæ of a few arsenites and arseniates.
16. How is phosphoretted hydrogen prepared, and what are its most striking properties? Give an equation.
17. Calculate how much $\mathbf{N}H_3$ by weight can be obtained upon ignition from 2·350 grms. of $\mathbf{P}O\ Amo\ Mgo''$.
18. Calculate the percentage composition of microcosmic salt.

CHAPTER XVII.

OXIDE OF BORON.

THE element *boron* occurs in nature always in combination with oxygen, as boric acid, either in the free state or combined with metals. The most important of its salts is *borax*, a compound of the base soda, with boric acid.

Experiment 85.—Dissolve a small quantity of powdered borax—the ordinary prismatic crystals of $\mathbf{B}_4O_5Nao_2$—in four times its weight of boiling water, and add to the filtered solution concentrated hydrochloric acid, till litmus-paper is freely reddened. *Orthoboric acid*, or *boric hydrate* separates on cooling in thin translucent pearly plates, which can be obtained in a sufficiently pure state, by pouring off the liquid, washing with a little water, spreading the crystals on filter-paper on a warm tile, and drying at a gentle heat. They are soluble in boiling water, to which they impart only a slight acid taste; and the solution of the acid gives to blue litmus-paper merely a wine-red tint similar to that which carbonic acid produces.

When treated with concentrated hydrochloric acid the sodoxyl radical, it may be assumed, is first acted upon with formation of sodic chloride and Ho_2. The five molecules of water (which may be viewed as hydride of hydroxyl, HHo), by attacking five atoms oxygen, form five molecules of Ho_2, and the hydrated acid separates, thus:—

$$\mathbf{B}_4O_5Nao_2 + 2HCl + 5\mathbf{O}H_2 = 4\mathbf{B}Ho_3 + 2NaCl.$$

The trihydric or tribasic acid, $\mathbf{B}Ho_3$, so obtained, is converted into the *metaboric acid*, $\mathbf{B}OHo$, by heating up to 100° C., thus:—

$$\mathbf{B}Ho_3 = \mathbf{B}OHo + \mathbf{O}H_2.$$

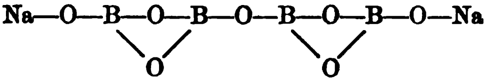
By exposing the acid to the strongest red heat we obtain *boric anhydride*. This cannot be done without incurring loss from volatilisation. The acid merely fuses and forms, on cooling, a glassy hard ringing mass. The composition of the anhydride is $\mathbf{B}'''_2O_3$, boron being a triad element. Its graphic formula is written—

$$O{=}B{-}O{-}B{=}O$$

Boric acid is principally derived from a mineral called *tincal*, an abnormal sodic borate, having the composition $\mathbf{B}_4O_5Nao_2$, $10\mathbf{O}H_2$, which may be viewed as a compound of two molecules of sodic metaborate and one molecule of boric anhydride—

$$2\mathbf{B}ONao + \mathbf{B}_2O_3 = \mathbf{B}_4O_5Nao_2.$$

Its graphic formula, as expressed by Dr. Frankland, is—



This view is borne out by the facility with which a dilute aqueous solution of borax is decomposed. On adding tincture of litmus to a concentrated borax solution, the liquid acquires a slightly reddish tint; which, on the addition of more water, turns distinctly blue: *i.e.*, on dilution the borax solution acts like a weak solution of a free alkali mixed with boric acid.

Boric acid combines with bases in the state of metallic hydrates, oxides, or carbonates, in many different proportions, both in the wet and dry way. Its salts are called *borates*. At high temperatures it behaves like a strong acid, displacing not only $\mathbf{C}O_2$, but $\mathbf{S}O_3$, and $\mathbf{P}_2O_5$, from their salts. In solution, however, boric acid is but a weak acid; although it is capable of combining with free bases and of decomposing, when in concentrated solutions the metallic carbonates, with evolution of $\mathbf{C}O_2$, especially on boiling. Its feeble acid character is also manifested in borates containing excess of acid—so-called acid salts—which react strongly alkaline, and in which the feeble acid cannot overcome the alkaline nature of such strong bases as soda or potassa.

Experiment 86.—Mix intimately in a mortar some of the boric acid obtained in Exp. 85 with somewhat less than its own weight of sodic chloride, and heat the mixture in a porcelain or platinum crucible over a good gas flame. The mass fuses and a vapour is given off. Remove the lamp for a moment, and hold an inverted bell-jar over the crucible. Strips of blue litmus, moistened with water, are made to adhere to the inside of the jar. As soon as the vapour comes in contact with the paper the blue colour changes to red. The vapour consisted of hydrochloric acid. This may be proved by rinsing the jar with a few drops of ammonia, before inverting it over the crucible, when white fumes of ammonic chloride are formed.

The change takes place according to the equation—

$$NaCl + \mathbf{B}Ho_3 = \mathbf{B}ONao + HCl + \mathbf{O}H_2.$$

Here, then, is another instance of a curious *reciprocal affinity*. Exp. 85 proved that boric acid is liberated from borax by concentrated hydrochloric acid. The preceding experiment showed that boric acid drives out hydrochloric acid. It is obvious, then, that the affinity of boric acid for soda is greater at a *high* temperature than that of hydrochloric acid; the different action of the two acids is evidently owing to the *fixed* character of the one, and to the *volatile* nature of the other acid—hydrochloric acid being volatile at the ordinary temperature. The tendency in the latter to volatilize at a high heat assisted its escape, whilst the fixedness of the boric acid was actually increased at a melting heat.

Most borates fuse to transparent glasses. Alkaline borates, when fused with metallic oxides, take up and dissolve many of the latter, forming double borates of the alkali base and the metallic oxide, which are frequently marked by characteristic colours. Hence borax is of great use as a *flux* in metallurgical experiments, or, on a small scale, in blowpipe reactions.

QUESTIONS AND EXERCISES.

1. What is our chief source of boric acid?
2. How is orthoboric acid obtained from borax? Give an equation.
3. Explain the action of heat upon orthoboric acid.
4. Give symbolic and graphic formulæ for orthoboric and metaboric acid, boric anhydride, borax.
5. What action takes place when orthoboric acid and sodic chloride, or potassic carbonate, are fused together?
6. What is the percentage of boric anhydride in borax?

CHAPTER XVIII.

ON THE BLOWPIPE AND ITS USE.

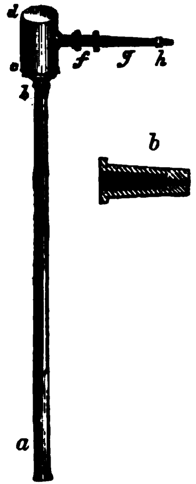


FIG. 59.

A useful blowpipe is represented in Fig. 59. It consists of three parts—of a straight tube made of brass or German silver, *a b* (sometimes fitted, for greater convenience, with a horn or ivory mouth-piece); of an air-chamber, *c d*, which arrests any condensed moisture; and of a branch tube, *f g*, which fits into the longer tube, *a b*, at a right angle. The tube, *f g*, is provided with a nozzle, *h*, ending in a platinum jet, which fits somewhat conically over the tube, *f g*, as is shown on a larger scale in Fig. 59, *b*. The most convenient form of mouthpiece is the trumpet-shaped, whereby blowing is rendered less fatiguing. Other simpler forms of blowpipes have been devised; they require, however, no special description to be readily understood.

The blowpipe is used for conveying a continuous blast of air from the lungs into the flame of a spirit-, gas-, or oil-lamp, or into a candle flame. In any ordinary conical flame we are able to distinguish three different parts, as represented in Fig. 60; 1st, in the middle a dark kernel, *a*; 2nd, a bright cone, *e f g*, surrounding the dark kernel, *a*; and 3rd, a feebly luminous outer cone, *b c d*, surrounding the bright cone. The dark part of the flame consists of vapours—principally of compounds of carbon and hydrogen—which burn at the expense of the oxygen of the air. The luminous zone of the candle flame does not get a sufficient supply of oxygen; it is, therefore, the hydrogen which burns chiefly, whilst the hydrocarbon vapour becomes highly heated, and is rendered luminous. In the outer or feebly luminous zone nothing impedes the free access of, and contact with, the atmospheric air; complete combustion takes place; both carbon and hydrogen are converted into their final products of oxidation, into carbonic anhydride and water (steam). This portion of the flame is very hot, the greatest heat being concentrated in the point *c*. If we hold a body, which is capable of taking up oxygen into this outer part of the flame, it becomes rapidly oxidized, since all the conditions are favourable to such a change, viz., a high temperature, and an unlimited supply of air.

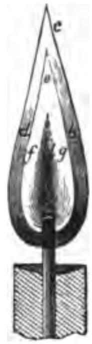


Fig. 60.

The outer zone of the flame forms, therefore, the *oxidizing* flame. If, on the other hand, we introduce a body which is capable of parting with oxygen, into the luminous part of the flame, we should expect to see it become deprived of its oxygen by the hydrocarbon vapours. The body is *deoxidized* or *reduced* in the luminous zone of the flame; hence this section is called the *reducing* flame.

Now, by introducing a current of air into the interior of a flame, the appearance of the flame changes immediately; it becomes shorter and more pointed in the direction of the current of air. The luminous portion of the flame disappears altogether, and the heat is considerably increased. Two zones of combustion are, in fact, formed by supplying air to the hydrocarbon vapours; from the inside, as well as from the outside. To produce either an oxidizing or reducing flame, the blast delivered from the blowpipe requires to be properly directed, and must be constant and regular.

While blowing, the trumpet-shaped mouth-piece is pressed *against* the lips, and breathing is effected through the nostrils; the epiglottis is used as a valve. The air must be forced through the blowpipe by the action of the muscles of the cheeks only.

"Beginners, when first practising with the blowpipe, usually commit the fault of not closing the passage between the windpipe and the mouth at the right moment, but of blowing for a longer or shorter period *from the lungs* alone. This mode of blowing, if persevered in, is undoubtedly prejudicial to health; and it is, therefore, advisable that the beginner should practise himself in breathing regularly and audibly through the nose, keeping up a continuous blast by the muscles of the cheeks. This practice should be continued till he is able to do so without any perceptible exertion.

In attempting this he will probably not be immediately successful, but a little practice will soon enable him to master this initial difficulty."—(*Plattner on the Blowpipe.*)

Success in blowpipe operations depends to a great extent upon the lamp we use.

In a laboratory which has a supply of coal-gas, a *Bunsen* burner of the construction shown in Fig. 61 will be found to answer extremely well. The burner rests on a foot of cast-iron, *a b*, into which a square (or round) block, *c d*, of brass or cast-iron is screwed. This has a cylindrical hole for conveying the air, drawn in through four holes, into the brass tube, *e f*, which screws either into or over the cylindrical hole. A branch tube, *k*, which can be connected by means of india-rubber tubing with the gas supply, conveys gas to a thin tube with a fine slit, or a couple of fine holes at its upper end, and is screwed into the cylindrical hole. The gas and air mix in the tube, *e f*, and burn at *f* with an almost non-luminous flame. The in-draught of cold air keeps the tube cool enough to prevent the flame striking back and burning at the small aperture below.

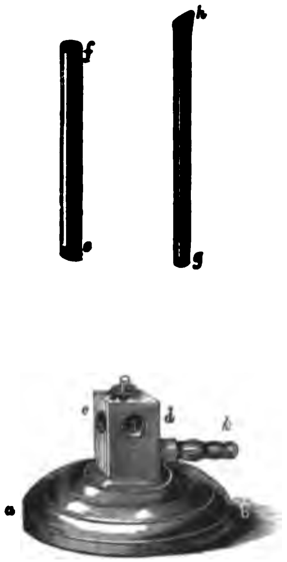


FIG. 61.

By introducing, for blowpipe purposes, a narrower tube, *g h*, flattened at the top, into the tube, *e f*, the gas is conveyed from the thin gas delivery-tube below without becoming mixed with air, and burns with its usual luminous flame. On directing a blowpipe jet into the gas flame, the latter is diverted, and we are enabled to produce either a reducing or an oxidizing flame.

In order to obtain a *reducing flame*, the nozzle (Fig. 62) of the blowpipe is held inclined, almost parallel with the surface of the flattened top of tube, *g h*, so as just to touch the exterior part of the flame. A more or less yellow flame will be thus produced of the form shown in Fig. 62.

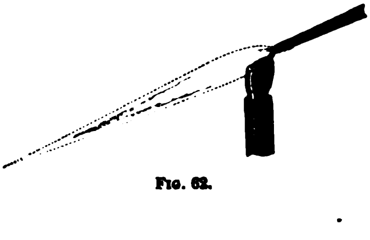


FIG. 62.

An *oxidizing* flame is obtained by keeping the nozzle of the blowpipe at the same inclination as before, but introducing it somewhat further into the flame (Fig. 63), so as to obtain a clear unbroken jet. A somewhat stronger blast is also sent into the flame, so as to produce a longer and more pointed jet of flame, of a pale blue colour, and almost invisible by daylight. If a *small* fragment of an oxidizable substance be held just *beyond* the point of this flame, it becomes intensely heated, and rapidly absorbs oxygen from the surrounding atmosphere, or,—if the blast from the blowpipe be very strong,—from the air which passed unconsumed through the centre of the flame.

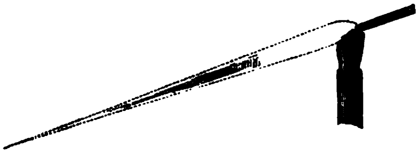


FIG. 63.

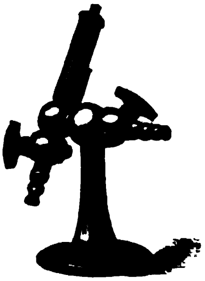


FIG 64.

When a substance is submitted to the action of the reducing flame, it should be held so as to be entirely surrounded by the yellow flame, and protected from the oxidizing action of the atmosphere, but as near as possible to the point of the flame, in order to utilize the greater heat of that part of the jet.

Far superior to a Bunsen gas-jet is *Herapath's* blowpipe lamp (Fig. 64), constructed on the principle of a Bunsen burner. The gas and air issue from the mouth of the brass jet *well mixed*, and burn, when lighted, with a blue flame. The flame can readily be rendered a reducing one, either by increasing the supply of gas, or by diminishing the blast; or an oxidizing one, by decreasing the gas and increasing the blast of air. By attaching the brass tube by means of flexible india-rubber tubing to a gas supply pipe, and connecting the air-tube with a short piece of tubing ending in an ivory or glass mouth-piece, the lamp becomes a highly serviceable piece of chemical apparatus.

Supports.—Charcoal is mostly used as a support in reduction experiments. The best charcoal is that from the wood of the pine, lime, or willow; closely grained, free from knots, and well burnt. The pieces are best cut by a small-toothed saw into regular prisms of about six inches in length, and from one to two inches in breadth, having a flat smooth surface at right angles to the lines of growth, because the fluxes spread out on the charcoal on the other surfaces (*Berzelius*). A good piece of charcoal may be made to serve for many experiments, by simply filing off the used surface and exposing a new one after each operation.

What renders charcoal so valuable as a support in blowpipe experiments is, 1st, its infusibility; 2nd, its weak power for conducting heat; 3rd, its porosity, which enables it to absorb within its pores readily fusible fluxes, such as borax, microcosmic salt, sodic carbonate, potassic cyanide, leaving the infusible substance under examination behind; and, lastly, its power of assisting in the reduction of oxidized substances in the inner blowpipe flame, on account of the carbonic oxide atmosphere which the charcoal furnishes by the partial combustion of its carbon.

The substance to be subjected to the blowpipe flame (which if a powder should be previously moistened with a little water to make it cohere) is placed in a shallow cavity, scraped out near the end of the charcoal, and the latter is so held that the flame impinges upon the substance at a slight angle, as seen in Fig. 58.

Platinum wire, frequently also *platinum foil*, or a small platinum spoon, is employed for oxidation experiments, or for the diffusion of insoluble bodies in fluxes, in order to observe the coloured glasses which they produce.

Thin platinum wire is chosen, which may be used in the form of a coil, with the ends unrolled, or in pieces about half a foot in length (Fig. 65). These are fused for convenience sake into a piece of glass tubing drawn out to a point, with the end turned into a hook or loop, to hold the borax or microcosmic salt which is to be fused into a bead. (Care must be taken that no substance, such as sulphur, lead, etc., which acts upon platinum, be fused upon the wire.)

Platinum foil is employed as a support for substances which are not to be exposed to the reducing action of charcoal. The foil may be placed on a piece of charcoal, or held in the flame by a pair of forceps.

Platinum Spoon.—This should be of the size and form shown in Fig. 66. It may either be fixed into a wooden handle or into a cork. (The lid of a small platinum crucible, supported on a platinum triangle (Fig. 67), answers equally well.) It is used for fusing certain substances with alkaline carbonates, hydric potassic sulphate ($\mathbf{S}O_2HoKo$), or nitre ($\mathbf{N}O_2Ko$).

FIG. 65.

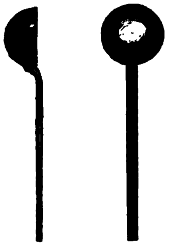


FIG. 66.

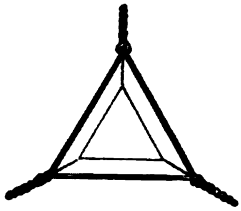


FIG. 67.

A pair of Brass Forceps with Platinum Tips.—These are constructed as shown in Fig. 68. A fragment of the mineral or other substance is held between the platinum points, *a*, which are opened by pressing on the knobs, *b b*, and close again by their own elasticity. These forceps are used for holding splinters of minerals, etc., which are to be heated in the outer or hottest part of the blowpipe flame, to ascertain their fusibility and the colour they impart to the blowpipe flame.

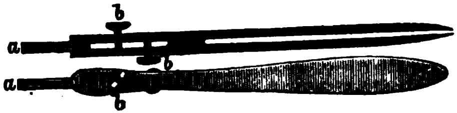


FIG. 68.

Experiment 87.—Heat on a charcoal support a little litharge (plumbic oxide, $\mathbf{Pb}O$) in the reducing flame of the blowpipe. Globules of metallic lead are left, and a yellow *incrustation* forms on that part of the charcoal over which the flame passes.

This arises from the deposition of yellow plumbic oxide on the cooler parts of the charcoal. Some of the metal is, in fact, volatilized, and on passing through the outer flame of the blowpipe is oxidized. The same occurs in the case of other metals; hence the different and often characteristic incrustations, observed when metallic oxides are heated on charcoal in the reducing flame, frequently help to distinguish such metallic bodies in a very ready manner.

Experiment 88.—Heat a small piece of metallic antimony in the cavity of the charcoal in the oxidizing flame of the blowpipe. The metal melts readily, and gives off white fumes, and a white deposit of antimonious oxide, $\mathbf{Sb}_2O_3$, covers the charcoal all round the metallic antimony, which by continued heat may be entirely volatilized.

Most metals (with the exception of gold and platinum) are capable of being converted into oxides, when heated in the outer flame of the blowpipe.

Experiment 89.—Melt some borax on the loop of the platinum wire to a clear pearl of borax glass. The bead should be perfectly colourless, both in the hot and cold state. While the glass is still hot and fluid, it is brought in contact with a small quantity of black cupric oxide, and the outer flame of the blowpipe applied a second time. The black oxide dissolves in the liquid glass, and produces a deep dark colour. If introduced in small quantities the glass is *green* whilst hot, and *blue* on cooling; if in large quantities the green colour is so intense as to appear black; when cool this becomes paler, and changes to a greenish-blue. When heated in the reducing flame the copper glass becomes nearly colourless, but immediately on solidifying assumes a red colour, and becomes opaque from the separation of metallic copper. By long continued blowing on charcoal the oxide is reduced, and the metal separates in the form of a small metallic bead, leaving the glass colourless.

The change which takes place will be readily understood after what has been stated in Chapter XVII with regard to the action of borax at high temperatures. The molecule $\mathbf{B}_2O_3$ forms with the $\mathbf{Cu}O$ a cupric metaborate, thus—

$$\mathbf{B}_2O_3 + \mathbf{Cu}O = \mathbf{B}_2O_4Cuo''.$$

In performing this experiment, and experiments of a similar nature, care must be taken not to dissolve, in the first instance, too large an amount of the oxide, or other substance under examination. If a small quantity affords no distinct reaction, more may be easily added. If, however, the colour of the bead be too intense to be clearly distinguishable, the bead may be jerked off from the wire, and the portion which still adheres fused up with a fresh quantity of borax, in which manner a more dilute bead will be obtained.

We possess in microcosmic salt another most valuable flux, as it leaves, on ignition, sodic metaphosphate, a readily fusible salt. The action of this salt is analogous to that of borax; but as experience has proved that the beads which it forms with many substances are more characteristic, and the colours better defined than those produced by borax glass, it is frequently preferred to the latter as a flux.

Microcosmic salt, when fusing at first in its eight molecules of water of crystallisation, is so fluid that it readily drops from the platinum loop. It is, therefore, advisable to fuse it on charcoal or platinum foil, when the water and ammonia are driven off, and a viscid residue is left. Some of the glass thus formed can readily be taken up on the platinum wire (the loop may be made somewhat smaller), and the powdered mineral or oxide fused with it in the same way as with borax.

Experiment 90.—Dissolve a little uranic oxide, U_2O_3, in a bead of microcosmic salt. It dissolves to a clear yellow glass in the outer flame, and becomes yellowish-green on cooling. Heated in the reducing flame the glass assumes a beautiful green colour, which becomes more brilliant as the bead cools.

The action of the sodic metaphosphate consists in taking up metallic oxides, and forming with them tribasic phosphates, containing more than one base.

The blowpipe is of great assistance in chemical analysis, because it individualizes the body under examination, by producing distinctive changes, which are peculiar for the most part to each of the metals. Although the presence of other bodies may interfere to some extent with the special reactions of the body for which we search, and thus render the search doubtful or in some cases nugatory, it cannot be too strongly impressed upon the chemical student to gain a complete mastery over the blowpipe reactions, as being by far the most easy and readily available means of qualitative analysis.

QUESTIONS AND EXERCISES.

1. Describe the construction of the mouth blowpipe.
2. Describe the nature of a candle flame.
3. Describe the construction of a *Bunsen* gas-burner.
4. Explain the oxidizing and reducing action of the blowpipe flame. Give examples.
5. Explain the use of borax and microcosmic salt in blowpipe reactions.

CHAPTER XIX.

ON SILICA AND SILICATES.

Silica is one of the most widely diffused substances in nature, and constitutes, together with the compounds which it forms with metallic bases, viz., the *silicates*, the greater part of the solid crust of our earth.

It is found either in the *free* or *combined* state. White and yellow sand, quartz, agate, flint, rock, crystal, opal, chalcedony, are more or less pure silica.

Experiment 91.—Add dilute hydrochloric, nitric, or sulphuric acid to a solution of so-called *water glass* (sodic silicate). Gelatinous silicic hydrate separates, which may be thrown on a filter and washed with water, in which medium it is but slightly soluble. Dry the precipitate by placing the funnel on a hot sand-bath over a filter drier (Fig. 69). The gelatinous mass shrinks together considerably. It loses its water and becomes anhydrous, even at the temperature of boiling water. Remove the precipitate, when dry, from the filter, and heat it strongly in a porcelain or platinum crucible. A fine white amorphous powder is left, perfectly insoluble in water.

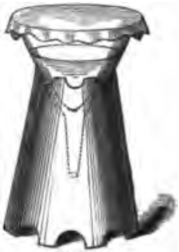


FIG. 69.

Analysis has proved that this white powder consists of one atom of the element silicon, and two atoms of oxygen; it is called silica, or *silicic anhydride*, $\mathbf{Si}O_2$. Silicon being combined with two atoms of oxygen, must be a tetrad element, and silica is written graphically—

$$O=Si=O.$$

Experiment 92.—Mix some *finely* powdered* quartz intimately with about four times its weight of *fusion mixture* ($\mathbf{C}ONao_2$ and $\mathbf{C}OKo_2$ mixed in atomic quantities) and heat in a covered platinum crucible over the flame of a Bunsen lamp. The mixture fuses, if sufficient heat be applied, and gives off bubbles of carbonic anhydride. Heat as long as any gas comes off, and keep the contents of the platinum crucible from ten minutes to a quarter of an hour in a state of quiet fusion; allow to cool, and remove the solidified mass from the crucible by digesting for some time with hot water in a porcelain dish. The whole of it dissolves. This proves that the quartz was completely fused. (A successful fusion can only be effected by powdering the quartz in the first instance very finely.) Acidulate the solution now with dilute hydrochloric acid; carbonic anhydride is evolved, owing to the decomposition of the excess of the alkaline carbonates, and gelatinous silica separates. Evaporate to complete dryness on a water-bath. Stir the gelatinous mass which is left with a stout glass rod, and break up the lumps. Transfer the dish for a short time to a hot sand-bath, and apply a somewhat stronger heat. Set it aside to cool, and treat with a few drops of concentrated hydrochloric acid. Allow the acid to soak for some time, and then add hot water. Filter the insoluble residue, wash well, dry and ignite gently in a porcelain or platinum crucible. A dazzling white powder of *silicic anhydride* will be left.

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* Hard substances, such as quartz, should be powdered in an agate mortar.

The changes may be expressed symbolically by the following equations:—

$$(1)\ 2\mathbf{Si}O_2 + 2(\mathbf{C}ONao_2,\mathbf{C}OKo_2) = \mathbf{Si}Nao_4,\mathbf{Si}Ko_4 + 4\mathbf{C}O_2.$$

Fusion mixture.

$$(2)\ \mathbf{Si}Ko_4 + 4HCl = \mathbf{Si}Ho_4 + 4KCl.$$

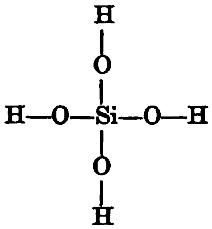
$$\mathbf{Si}Nao_4 + 4HCl = \mathbf{Si}Ho_4 + 4NaCl.$$

Silicic hydrate.

$$(3)\ \mathbf{Si}Ho_4 = \mathbf{Si}O_2 + 2\mathbf{O}H_2.$$

Silicic anhydride.

Silicic acid (also called orthosilicic acid) is a *tetrabasic* acid, being combined with four atoms of Ho. It is written graphically—



$$\begin{array}{ccccccc} & & & H & & & \\ & & & | & & & \\ & & & O & & & \\ & & & | & & & \\ H & - & O - & Si & - O & - & H \\ & & & | & & & \\ & & & O & & & \\ & & & | & & & \\ & & & H & & & \end{array}$$

A *dibasic* acid is said to be produced by the evaporation *in vacuo* at 16° C., of a solution of the tetrabasic acid in water—

$$\mathbf{Si}Ho_4 = \mathbf{Si}OHo_2 + \mathbf{O}H_2.$$

This acid is of little interest.

Silicic acid is an extremely indifferent body; it is inodorous and tasteless, and has scarcely any action upon vegetable colours (litmus). It combines with bases in the wet way with great difficulty, and forms amorphous salts. Like boric acid it is affected quite differently at a high temperature.

Experiment 93.—Heat a mixture of powdered nitre ($\mathbf{N}O_2Ko$) with finely powdered quartz in a platinum crucible over a good gas flame; ruddy fumes are seen to escape. The nitric anhydride is displaced by the silicic anhydride, and breaks up as soon as it is liberated from the nitre into $\mathbf{N}_2O_4$ and O.

Silicic anhydride, therefore, liberates nitric anhydride from its salts. A similar action takes place when sodic chloride is employed instead of nitre. $\mathbf{Si}O_2$ can even drive out $\mathbf{S}O_3$ (*e.g.*, from $\mathbf{S}O_2Nao_2$), especially when heated with it in the presence of charcoal; and yet in Exp. 90 it has been shown that silicic hydrate can be separated from sodic silicate by dilute hydrochloric acid.

Silica, in this respect, resembles boric acid. It exhibits at *different temperatures* the same curious *reciprocal affinity*, for it can be displaced from its saline combinations by hydrochloric acid, etc., or may itself displace at a high temperature,—owing to its fixed character,—volatile acids, such as carbonic, nitric, hydrochloric,* sulphuric acid. On passing carbonic anhydride through a solution of sodic silicate, gelatinous silicic acid separates in flakes.

The reaction takes place according to the equation—

$$\mathbf{Si}\mathrm{Nao}_4 + 4\mathbf{C}\mathrm{O}_2 + 4\mathbf{O}\mathrm{H}_2 = \mathbf{Si}\mathrm{Ho}_4 + 4\mathbf{C}\mathrm{OHoNao}.$$

Hydric sodic carbonate.

It is, no doubt, owing to this action of carbonic anhydride upon silicates, that many spring waters contain small quantities of silicic acid in solution.

Different kinds of glass, colourless or coloured, may be made on a small scale by fusing before the blowpipe flame a *small* quantity of sodic carbonate, together with some white SiO_2, and by dipping the clear bead into various metallic oxides, and heating once more.

Porcelain, fire-clay, bricks, tiles, stone-ware, pottery, etc., consist mainly of aluminic silicate.

A great many minerals consist of silica and earthy and metallic bases in varying proportions.

QUESTIONS AND EXERCISES.

1. How does silica occur in nature?
2. How can silicic anhydride be prepared from a solution of water-glass?
3. How is white sand converted into potassic silicate?
4. Give symbolic and graphic formulæ for silicic anhydride and silicic acid.
5. How would you show experimentally that silica can displace $\mathbf{N}_2\mathrm{O}_5$ or $\mathbf{S}\mathrm{O}_3$ from their respective sodic salts?
6. Explain the action of $\mathbf{C}\mathrm{O}_2$ upon a weak solution of sodic silicate.
7. What substances enter chiefly into the composition of porcelain, fire-clay, stone-ware?
8. How much $\mathbf{Si}\mathrm{O}_2$, and how much $\mathbf{C}\mathrm{ONao}_2$ are required to manufacture 100 lbs. of water-glass?
9. 1·235 grm. of fire-clay yielded ·793 grm. of $\mathbf{Si}\mathrm{O}_2$, what is the percentage of silica in the clay?

CHAPTER XX.

GENERAL PROPERTIES OF SALTS.

The *solubility* of different salts in water varies very much. Some salts, such as calcic chloride, $\mathbf{Ca}\mathrm{Cl}_2$, magnesic chloride, $\mathbf{Mg}\mathrm{Cl}_2$, cannot be left exposed to the air even, without attracting moisture very rapidly; they are deliquescent. Others, such as calcic carbonate, $\mathbf{C}\mathrm{OCao}''$, have no attraction for water. Certain salts dissolve in water, others are insoluble. Almost all salts which are soluble in water, dissolve more freely and more extensively in boiling than in cold water. A solution is said to be *saturated in the cold,* when no more of the salt dissolves in it; a *hot saturated* solution, when boiling water has dissolved as much of a salt as will dissolve.

---

* By heating the mixture of SiO_2 and NaCl in a current of steam.

Experiment 94.—Dissolve some common salt in hot water in a porcelain dish, and raise the temperature at last to boiling. Plunge a thermometer into the liquid. The mercury rises rapidly above 100° C.—the temperature of boiling water. A *saturated* boiling solution of NaCl indicates in fact a temperature of 108—109° C.

The boiling point of saturated solutions, and the percentage of solubility of a few well known salts, are here annexed—

Name of salt.	Parts by weight of salt dissolved in 100 parts of water.	Boiling point of saturated solution.
Potassic chlorate	61·5	104·2° C.
Baric chloride	60·1	104·4° "
Sodic carbonate	48·5	104·6° "
Potassic chloride	59·4	108·3° "
Sodic chloride	41·2	108·4° "
Ammonic chloride	88·9	114·2° "
Potassic nitrate	335·1	115·9° "
Strontic chloride	117·5	117·8° "
Sodic nitrate	224·8	121·0° "
Potassic carbonate	205·0	135·0° "
Calcic nitrate	362·0	151·0° "
Calcic chloride	325·0	179·5° ".

It appears that in most instances the boiling point is directly proportionate to the solubility of a salt.

On allowing a saturated boiling solution to cool, some of the salt *crystallises* out, and the crystals will be all the more perfect the slower the solution cools. In order to get good crystals, saline solutions are set aside for spontaneous evaporation. The solution should, of course, be well protected from dust, by being kept carefully covered with filter-paper. In consequence of the constantly increasing concentration of the saline solution by slow evaporation in the air, the crystals have plenty of time to form regularly, and to grow slowly, till at last nearly the whole of the salt has been withdrawn from the solution. The remaining liquid may then be poured off from the crystals; it is called the *mother-liquor.* Growing crystals may actually be fed with a fresh portion of the saline solution, till they have acquired a considerable size.

Experiment 95.—Make a hot saturated solution of the well known salt *alum.* Allow it to cool. Then pour off from the crystals the still warm mother-liquor into a previously warmed porcelain dish, and set aside for crystallisation. When cold, pour off the mother-liquor, and pick out a few of the best crystals. They are *octohedral* in shape. One or more of these octohedra are then put into the cold saturated mother-liquor, and the crystal turned over on a fresh side every day, till after eight days it has rested on every one of the eight sides. It grows during this time, and attains considerable size, whilst the form of crystallisation remains the same.

If the crystal were not turned, it would likewise grow, but not regularly; for no deposit of saline matter can take place on the side on which it lies, nor on the side diametrically opposite to it. It would acquire what is called the *truncated octohedral* form. Instead of turning the crystals over, day after day, they may be allowed to form on a piece of fine string, from which they are conveniently suspended in the mother liquor, and left to grow slowly.

Crystallisation furnishes us with the means of *purifying soluble salts* from foreign substances. It is easy to purify salts soluble with difficulty from salts which dissolve freely in water, such as potassic carbonate, calcic chloride. Smaller crystals, as a rule, are purer than large crystals, because some of the mother-liquor is apt to be locked up within the interstices of the latter. Thus commercial nitre or saltpetre contains small quantities of potassic chloride and sulphate, which can only with difficulty be removed by repeated recrystallisation: but they are readily eliminated by constantly stirring a hot solution of the impure salt whilst it cools, as long as a fine powder (called *saltpetre flour*) of potassic nitrate falls out. The impurities are left in the mother-liquor.

Many salts combine chemically, the moment they crystallise, with a certain quantity of water, called *water of crystallisation*. This appears to be essential to their existence in a crystalline condition, and materially influences their structure; for on expelling the water by heat, the crystals crumble down to a powder. The anhydrous powder attracts water again very eagerly, and such dehydrated salts are frequently employed to deprive certain liquids, such as spirits of wine, etc., of water.

A great number of salts unite with the same amount of water of crystallisation under identical conditions of temperature and saturation: and the molecular units of water of crystallisation are reducible to simple constant proportions, and follow the law of constant chemical combining proportions, as much as compounds of two or more elements.

Experiment 96.—Heat a few grammes of *blue vitriol*, or cupric sulphate ($SOHo_2Cuo''$, 4 aq.) cautiously in a porcelain dish. The salt fuses in its water of crystallisation, or it undergoes what is called the *aqueous fusion*. It is dihydric at about 100° C. Keep stirring with a glass rod, till the water of crystallisation has been driven off, and till the blue salt has nearly turned white. On adding a little water to a portion of the powder, and stirring, it acquires its blue colour again. Much heat is given off at the same time.

Experiment 97.—To another portion of the white powder add a little alcohol (methylated spirit). The blue colour is likewise restored. The alcohol must have become deprived of its water. In this manner weak alcohol may be rendered almost *absolute*, *i.e.*, free from water.

The *evolution* of *heat* which accompanied the combination of the white powder with water, points to an actual *chemical* combination between the water of crystallisation and the salt.

On exposing the white powder to a stronger heat (about 200° C.), another molecule of water is given off, which is evidently combined differently from the four molecules of water of crystallisation. It is termed *water* of *constitution*.

The water of crystallisation of a salt, obtained from one and the same saturated solution, frequently varies with the temperature: *e.g.*, sodic sulphate ($\mathbf{S}O_2Nao_2$) when allowed to crystallise from its solution at a temperature of 33° C., retains ten molecules of water, and yields anhydrous crystals above that temperature.

Manganous sulphate ($\mathbf{S}O_2Mno''$) crystallises from its aqueous solution with six molecules of water of crystallisation at 15° C. It has the composition $\mathbf{S}OHo_2Mno'' + 6$ aq. Between 15° C. and 30° C. it crystallises with five, and between 30° C. and 40° C. with four molecules of water of crystallisation. The crystals belong respectively to the rhombic, triclinohedric, and monoclinohedric systems. It follows that the molecules of water of crystallisation are capable of modifying the character of salts as much as their other constituent elements. The last molecule of water—the water of constitution—is only driven off at 200° C.

Experiment 98.—Expose a few crystals of *washing soda* ($\mathbf{C}ONao_2 + 10$ aq.), for some time to the air. They become opaque, and crumble at last to pieces. The salt loses its water of crystallisation, even at the common temperature, but more rapidly when gently heated.

The same is observed when *green vitriol* ($\mathbf{S}OHo_2Feo'' + 6$ aq.), hydric disodic phosphate ($\mathbf{P}OHoNao_2 + 12$ aq.), sodic sulphate ($\mathbf{S}O_2Nao_2 + 10$ aq.), and other similarly constituted salts are exposed to the air. These salts are said to be *efflorescent*.

Salts which have been allowed to crystallise from water at the ordinary temperature, and have consequently taken up as much water of crystallisation as they possibly can,—produce *cold*, when their crystals are redissolved, either at the same or at a higher temperature; because they absorb heat from the water on passing from the solid to the liquid state. Heat must, therefore, have become transferred, in the one instance, from the dehydrated salt to the water (which has already as much heat as it can bind), and heat is therefore given off: in the other instance from the water to the crystalline salt, the latter depriving the water of heat. On mixing some salts or a mixture of certain salts in definite proportions with water, a considerable degree of *cold* may be produced. Mixtures of this kind are called *freezing mixtures*.

Experiment 99.—Mix one part by weight of crystallised sodic carbonate with one part by weight of water at 10° C., and ascertain by the aid of a thermometer that the temperature of the water is lowered from 10° C. to − 14° C.

Numerous other salts may be employed with like effect.

Colour of Salts.—Most salts are *solid* bodies at an ordinary temperature. Salts obtained by the action of a colourless acid upon a colourless base are likewise *colourless*. Coloured bases produce for the most part coloured salts on combining with colourless acids; and the crystalline salts mostly resemble the original base in colour. Salts formed by the combination of a colourless base with a coloured acid generally exhibit the colour of the acid from which they are derived.

Taste of Soluble Salts.—The taste which various salts exhibit is for the most part dependent upon the constituent base. Thus, sodic salts possess a purely saline taste, not unlike that of common salt; potassic salts possess a saline, and somewhat bitter taste. Magnesic salts have a nauseous bitterness; aluminic salts an astringent sweet taste, etc. The taste is also influenced by the acid which the salts contain, as in sulphites and salts of metallic acids.

QUESTIONS AND EXERCISES.

1. Give instances of deliquescent salts.
2. How would you prepare a saturated solution of a salt?
3. What general relation is there traceable between the solubility of salts and the boiling points of their saturated solutions? Give instances.
4. How are salts soluble in water purified?
5. Explain the terms *mother-liquor*, *aqueous fusion*, *water of constitution*, *efflorescent*, *freezing mixture*.
6. How would you prepare octohedral crystals of alum?
7. How is saltpetre freed from potassic chloride and sulphate?
8. Give the symbolic formulæ of blue vitriol, green vitriol, crystallised manganous sulphate.
9. Explain what takes place when blue vitriol is heated—1st, to 100° C.; 2nd, to 200° C.
10. What is the action of dehydrated cupric sulphate upon ordinary proof spirits (containing 50 per cent. of alcohol)?
11. On what considerations would you select the materials for making a freezing mixture?
12. Explain the cause of the colour which various salts exhibit.
13. What influences the taste of salts?
14. How would you determine experimentally the percentage of water of crystallisation in a salt?
15. Three grms. of washing soda lost 1·888 grm. of water on drying and ignition: what is the percentage of water of crystallisation, and how would you calculate the formula of the crystalline salt from these numbers?

CHAPTER XXI.

REACTION OF SALTS.—NORMAL, ACID and BASIC SALTS.—DOUBLE SALTS.

On adding a solution of potassic hydrate to sulphuric acid (comp. Exp. 60), we obtained a *salt* which was *neutral* to litmus paper,[*]

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[*] Litmus is a vegetable colouring matter consisting of a true salt of a mineral base and a vegetable acid. On adding to a solution of litmus in water a mineral acid, the organic salt is decomposed, and the organic acid liberated. This acid possesses great tinctorial power, and is of a light red colour. A weak acid deprives the blue salt only of one-half of its base; leaving a salt, containing excess of the organic acid, and imparting to the solution a peculiar wine-coloured tint. On the addition of a soluble base, the red solution turns blue again, because the base combines with the acid to form a blue salt.

A sensitive litmus solution should not, therefore, contain any free base, because acids would first neutralize this latter before they could liberate the *i.e.*, it did not turn blue litmus red nor red litmus blue. Now, potassic hydrate has a strongly alkaline, and sulphuric acid a strongly acid reaction: and it would, therefore, appear as if one of the most characteristic signs of the *saline* nature of a body consisted in its neutral reaction. This applies, however, only to a very limited number of salts, such as potassic nitrate ($\mathbf{N}O_2Ko$), sodic nitrate ($\mathbf{N}O_2Nao$), sodic sulphate ($\mathbf{S}O_2Nao_2$), magnesic sulphate ($\mathbf{S}O_2Mgo''$), calcic sulphate ($\mathbf{S}O_2Cao''$), baric nitrate ($(\mathbf{N}O_2)_2Bao''$). By far the greater number of salts, in fact most soluble sulphates and nitrates, have the power of reddening blue litmus, *e.g.*, ferrous sulphate ($\mathbf{S}O_2Feo''$), zincic sulphate ($\mathbf{S}O_2Zno''$), manganous sulphate ($\mathbf{S}O_2Mno''$), cupric sulphate ($\mathbf{S}O_2Cuo''$). Others, again, turn red litmus paper blue; *e.g.*, sodic and potassic carbonates, borax, etc. Hence there are salts which react *neutral;* others which react *acid* or *alkaline*, and in which the acid reaction does not arise from any *free* or *uncombined acid* in the salt, nor the alkaline reaction from any *free alkali*, but in which the reaction is due rather to the relative *strength* of the acid and basic constituents which make up the saline body.

The powerful sulphuric acid, for instance, can only just neutralize the strong alkali, potassa; and when in combination with weaker bases, such as the oxides of the metals proper (which, as we have seen repeatedly, are without reaction on litmus-paper), it impresses its acid character upon the salts. The same applies to the salts which nitric and other mineral acids form.

Weak acids, such as carbonic, boric, and silicic acid, on the other hand, are not capable of entirely neutralizing strong alkaline bases, such as potassa and soda: their saline compounds react alkaline. It is impossible, therefore, to infer the preponderance of acid or base in a salt from the reaction, if any, which it possesses; for in solutions of salts, such as—

$$\mathbf{S}O_2Nao_2, \quad \text{and} \quad \mathbf{S}O_2Cuo''.$$

Sodic sulphate (neutral).	Cupric sulphate (acid).

—salts which exhibit neutral and acid reactions, and which are formed by the displacement of the hydrogen of the sulphuric acid by atomic amounts of the metals sodium and copper,—the same amount of acid causes the one salt to become neutral, the other acid.

If we take a *salt*[*] to be the product of the mutual action of an acid and a metal or base upon each other, **normal** *salts are obtained by exchanging the whole of the replaceable hydrogen of the acid for an equivalent amount of a metal, or of a positive compound radical, such as ammonium,* NH_4.

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acid contained in litmus. A solution of red litmus is obtained by adding very dilute sulphuric acid, by means of a glass rod, till the blue of the litmus is changed to a distinct red. Such a solution is turned blue on coming in contact with the least trace of a soluble base.

[*] Frankland: Lecture Notes, page 12.

Instances of normal salts:—

Salts.	Acid from which the salts are derived.
$\mathbf{N}O_2Ko$, neutral reaction............	$\mathbf{N}O_2Ho$.
$\mathbf{S}O_2Nao_2$, „ „	$\mathbf{S}\,O_2Ho_2$.
$\mathbf{S}O_2Cao''$, „ „	$\mathbf{S}O_2Ho_2$.
$(\mathbf{N}O_2)_2Coo''$, acid reaction	$\mathbf{N}O_2Ho$.
$\mathbf{N}OKo$, alkaline reaction............	$\mathbf{N}OHo$.
$\mathbf{S}O_2Zno''$, acid reaction	$\mathbf{S}\,O_2Ho_2$.
$\mathbf{P}ONao_3$, alkaline reaction	$\mathbf{P}OHo_3$.
$(\mathbf{P}O)_2Cao''_3$ (insol. in water)	$\mathbf{P}OHo_3$.
$\mathbf{B}Nao_3$, alkaline reaction	$\mathbf{B}Ho_3$.
$\mathbf{Si}Nao_4$, „ „	$\mathbf{Si}Ho_4$.

An **acid** *salt is obtained when two or more atoms of replaceable hydrogen are only partially exchanged for the metal or positive compound radical.*

The following are illustrations of acid salts—

Salt.	Acid.
$\mathbf{S}O_2HoKo$, acid reaction............	$\mathbf{S}O_2Ho_2$.
$\mathbf{C}OHoKo$, alkaline reaction	$(\mathbf{C}OHo_2)$?
$\mathbf{P}OHoNao_2$, alkaline reaction........	$\mathbf{P}OHo_3$.
$\mathbf{As}OHoKo_2$, alkaline reaction	$\mathbf{As}OHo_3$.
$\mathbf{S}OHONao$, acid reaction	$\mathbf{S}OHo_2$.

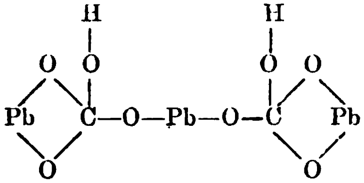
Monobasic acids form normal salts. Di-, tri-, and tetra-basic acids only can form acid salts. Dyad elements replacing H_2 in dibasic acids exclude the possibility of acid salts, unless two molecules of acid enter into the reaction.

The reaction with litmus is obviously no criterion of the normal or acid constitution of a salt.

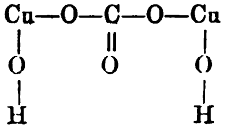
"*When the number of bonds of the metal or compound positive radical in a salt exceeds the number of atoms of displaceable hydrogen in the acid, the compound is usually termed a* **basic** *salt,*" ex. gr.

Symbolic formulæ. *Graphic formulæ.*

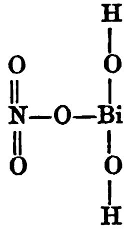
Ordinary white lead. $\left.\begin{matrix}\mathbf{C}HoPbo'' \\ \mathbf{C}HoPbo''\end{matrix}\right\} Pbo''$



Malachite, Dicupric carbonate dihydrate. $\mathbf{C}O(OCu''Ho)_2$.



Bismuthous nitrate dihydrate. $\left.\right\} \mathbf{N}O_2(OBi'''Ho_2)$



Double Salts.—There exists a class of salts called double salts, containing *one* acid only, but *two different* bases, and quite distinct from the acid salts just explained. The base ammonia is especially remarkable for its tendency to form double salts.

Chemists are compelled to admit in these double salts, and in salts containing water of crystallisation, a mere *molecular union* or *molecular combination.* This, in chemical notation, is distinguished from atomic combinations by the use of the comma. In all cases molecular combination seems to be of a much more feeble character than atomic union.

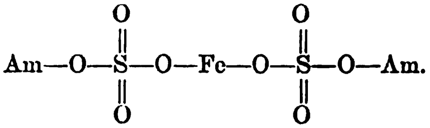
The following are instances of double salts, in which a mere molecular combination is traceable—

$$\begin{array}{l} AmCl,\ MgCl_2 + 6OH_2. \\ 2AmCl,\ Fe_2Cl_6 + 3OH_2. \\ 2AmCl,\ SnCl_4 + OH_2. \\ 2KCl,\ ZnCl_2. \end{array}$$

Other double salts are formulated atomically, thus—

Symbolically. *Graphically.*

$$\begin{array}{l} \mathbf{S}O_2Amo \\ \mathbf{S}O_2Amo \end{array} Feo'',\ 6\mathbf{O}H_2.$$



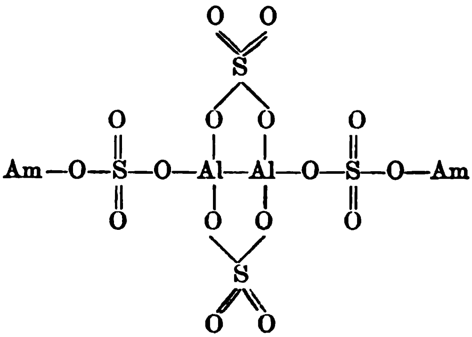
In like manner an important group of double salts is formed by the combination of the sulphates of the metals aluminium, chromium, iron, manganese, with the alkaline sulphates. They have received the name of *alums*, from the resemblance which they have to common alum, a salt, known long before the others were prepared.

Examples of alums we have in—

Common ammonium alum (Diammonic aluminic tetrasulphate).

$$\begin{array}{l} \mathbf{S}O_2Amo\rceil \\ \mathbf{S}O_2 = \\ \mathbf{S}O_2 = \\ \mathbf{S}O_2Amo\rfloor \end{array} Al_2o^{vi},24\mathbf{O}H_2.$$

Graphic formula.



Potassium Iron Alum (Dipotassic ferric tetrasulphate).

$$\left.\begin{array}{l}SO_2Ko-\\SO_2=\\SO_2=\\SO_2Ko-\end{array}\right]Fe_2o^{vi},24OH_2.$$

Potassium Chrome Alum (Dipotassic chromic tetrasulphate).

$$\left.\begin{array}{l}SO_2Ko-\\SO_2=\\SO_2=\\SO_2Ko-\end{array}\right]Cr_2o^{vi},24OH_2.$$

These double salts are remarkable for the facility with which they crystallise and for the size and beauty of their crystals.

QUESTIONS AND EXERCISES.

1. Give instances of salts which react neutral acid or alkaline with litmus-paper; and assign reasons for the reaction which different salts give.
2. Define normal, acid and basic salts; give instances of each class of salts.
3. Why can litmus not be employed, in order to ascertain whether a salt is a normal or acid salt?
4. What is a double salt?
5. Give instances of double salts in which only a molecular combination can be traced.
6. Enumerate some double salts in which an atomic union is apparent.
7. What is an alum? Give names, as well as symbolic and graphic formulæ of different alums.
8. Write out the symbolic and graphic formulæ for hydric sodic sulphite, white lead, and *malachite*.
9. Explain in what combination water of crystallisation is considered to exist in salts.
10. You have given to you hydric potassic sulphate and saltpetre. Explain how you would demonstrate experimentally that one of these salts is an acid salt.

CHAPTER XXII.

DEFINITION OF CHEMISTRY.—MODES OF CHEMICAL ACTION.

CHEMISTRY has been defined as "the science which treats of the composition of all kinds of matter, and of those changes in composition which result from the action either of different kinds of matter upon each other, or of external forces upon one and the same kind of matter."[*]

Chemical changes depend upon the affinities with which every kind of matter has been endowed by nature: they are modified more or less by the temperature, and by the state of aggregation—solid, liquid or gaseous—of the simple or compound bodies.

Matter undergoes a chemical change[†]—

I. When an element combines with another element in simple or multiple proportions, to form a compound body: *e.g.*,

$$Hg + O = HgO \text{ (Exp. 7)},$$
$$Sb_2 + O_3 = Sb_2O_3 \text{ (Exp. 88)},$$

or, **when an element or a compound body combines with a compound, to form a more or less complex compound body:** *e.g.*,

$$O + SO_2 = SO_3.$$
$$NH_3 + HCl = NH_4Cl \text{ (Exp. 72)}.$$

One of the most important groups of bodies, viz., the **metallic oxides**, is formed by the combination of metals with oxygen—a chemical change which is a true process of *combustion*, accompanied by the evolution of much heat. The following are the conditions which are most favourable to such a change:—

1st. The *metal should be in a finely divided state; e.g.*, in the form of powder, or as thin wire or foil.

Copper wire, or thin zinc foil, burns in a Bunsen gas flame; *i.e.*, the metals combine with oxygen to form cupric and zincic oxide. Iron obtained by the reduction of ferric oxide, in a current of dry hydrogen gas—so called pyrophoric iron—is oxidized by air at the ordinary temperature.

2nd. *A metal which forms a fusible oxide burns more readily*, because a fresh surface of unoxidized metal is constantly exposed to the oxygen.

3rd. *A volatile metal, i.e.*, a metal which can be readily converted into vapour, such as sodium, zinc, cadmium, *combines with oxygen more readily than a metal with difficulty volatilized*, such as silver, copper; because the two elements are brought together in the gaseous state, and the contact between their particles is thereby greatly promoted.

4th. *Many metals which at the ordinary temperature are not acted upon by*

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[*] Frankland: Lecture Notes, page 1.

[†] *A change arising from the rearrangement of the elements, or groups of elements, already contained in a body*, so as to form *isomeric* compounds, occurs very rarely among inorganic bodies, and may be neglected altogether.

dry air, are rapidly oxidized in a moist atmosphere, containing traces of carbonic anhydride.

Iron, for example, rusts rapidly in moist air.

Zinc is protected, after a time, by a film of white oxide. Both these metals oxidize far more rapidly when exposed to acid fumes. Tin plate, *i.e.*, iron coated over with a layer of tin, in order to protect it from rusting, is rapidly destroyed as soon as the tin coating has become damaged in places, because a voltaic action is set up between the metals tin and iron and the oxygen.

Iron filings placed in a saucer and moistened with water, are for some time left exposed to a moist atmosphere. They soon become covered with red iron rust. The oxidation proceeds at first slowly, at the expense of the oxygen in the air which the water holds in solution, but goes on more rapidly after the metal has become covered with a coating of iron oxide. A faint odour of hydrogen is likewise observed; because the iron forms the electro-positive pole of a voltaic pile—

$$\overset{+}{\mathrm{Fe}} \qquad \overset{-}{\mathrm{O}}$$

Water is thus decomposed at the ordinary temperature, and the iron is oxidized simultaneously by the oxygen of the air, dissolved in the water, and by the oxygen of the water itself.

Lower oxides, *e.g.*, ferrous or manganous oxide, are rapidly converted into *higher* oxides, by the action of the oxygen in atmospheric air, especially in the presence of water, or when they exist already as hydrates—

$$\underset{\substack{\text{Ferrous}\\ \text{hydrate.}}}{2\mathbf{Fe}''\mathrm{Ho}_2} + \mathrm{O} + \mathbf{O}\mathrm{H}_2 = \underset{\substack{\text{Ferric}\\ \text{hydrate.}}}{\mathbf{Fe}_2\mathrm{Ho}_6}.$$

$$\underset{\substack{\text{Manganous}\\ \text{hydrate.}}}{2\mathbf{Mn}''\mathrm{Ho}_2} + \mathrm{O} = \underset{\substack{\text{Manganic}\\ \text{hydrate.}}}{\left\{\begin{matrix}\mathbf{Mn}\mathrm{OHo}\\ \mathbf{Mn}\mathrm{OHo}\end{matrix}\right.} + \mathbf{O}\mathrm{H}_2.$$

Other lower oxides require to be heated in contact with air; $\mathbf{Pb}\mathrm{O}$, for instance, when heated to 400° C., combines with oxygen to form red lead, $\mathbf{Pb}_3\mathrm{O}_4$—

$$3\mathbf{Pb}\mathrm{O} + \mathrm{O} = \mathbf{Pb}_3\mathrm{O}_4,$$

but yields its oxygen again when heated more strongly,—

$$\mathbf{Pb}_3\mathrm{O}_4 = 3\mathbf{Pb}\mathrm{O} + \mathrm{O}.$$

Combination and **resolution** being, in this instance, merely a question of temperature.

5th. *Many metals whose oxides combine with alkali bases, and play the part of an acid, are all the more rapidly acted upon by oxygen* when in contact with alkalies, or in the presence of the vapour of ammonia.

Experiment 100.—Fill a test-tube with oxygen and bright copper turnings, and invert it over a small dish containing a strong solution of ammonia. The colourless liquid becomes gradually blue, and is seen to rise slowly in the tube, till the whole test-tube is filled with it.

Copper is but little acted upon by moist atmosphere; not so, however, when placed in a gaseous mixture containing oxygen and ammonia. The chemical change is induced by the tendency of cupric oxide to dissolve in ammonia to a blue liquid, and to form a chemical compound of a quasi-saline nature:—

$$\mathbf{Cu}\mathrm{O} + 2\mathrm{AmHo} = \underset{\substack{\text{Ammonic}\\ \text{cuprate.}}}{\mathbf{Cu}\mathrm{Amo}_2} + \mathbf{O}\mathrm{H}_2.$$

Metals may be divided, according to the facility with which they become oxidized and displace hydrogen in water, as follows :—

Metals whose oxides are not decomposed by heat alone.				**Metals whose oxides are decomposed by heat alone.**
I. **Metals** which combine with oxygen at all temperatures, and which decompose water at the lowest temperature, with evolution of hydrogen.	II. **Metals** which combine with oxygen only at an increased temperature, and which decompose water at 100° C., or, in the presence of an acid, in the cold, hydrogen being given off. Some (Al, Zn, Cd) decompose potassic hydrate, with evolution of hydrogen.	III. **Metals** which combine with oxygen at a red heat, and which decompose water (steam) at a red heat; but are not oxidized by water in the presence of strong acids. Their oxides act as acids in the presence of strong alkali bases. Tin decomposes potassic hydrate, on boiling, with evolution of hydrogen.	IV. **Metals** which combine with oxygen at a red heat, and decompose water (steam) to a slight degree, and only at a very high temperature. They do not decompose water in the presence of strong acids or alkalies at the ordinary temperature.	V. **Metals** which do not combine with oxygen directly, and which do not decompose water under any conditions. They are sometimes called *noble* metals.
Potassium. Sodium. Barium. Strontium. Calcium.	Magnesium. Aluminium. Manganese. Iron. Chromium. Nickel. Cobalt. Zinc. Cadmium.	Tin. Antimony.	Copper. Lead. Bismuth.	Mercury. Silver. Platinum. Gold.

The power which metals possess of combining with **sulphur, chlorine,** &c., varies likewise greatly in degree and intensity, according to the nature and state of division of the metal, and according to temperature. Most metals, as we have seen in Chapters VII and VIII, combine directly with chlorine and sulphur, and their respective chlorides and sulphides resist decomposition by heat, with the exception of those of the noble metals, gold and platinum.

Matter undergoes a chemical change—

II. When a compound body resolves itself into its component elements; or into an element and a compound body; or, lastly, **into two or more, less complex compound bodies :** *e.g.*,

$$\begin{aligned}
\mathbf{Hg}\mathrm{O} &= \mathrm{Hg} + \mathrm{O} \quad \text{(Exp. 8).}\\
3\mathbf{Fe}^{\mathrm{iv}}\mathrm{S}_2 &= \mathbf{Fe}_3\mathrm{S}_4 + \mathrm{S}_2 \quad \text{(Exp. 40).}\\
\mathbf{N}\mathrm{O}_2\mathrm{Amo} &= \mathbf{O}\mathrm{N}_2 + 2\mathbf{O}\mathrm{H}_2 \; \text{(Exp. 70).}\\
(\mathbf{N}\mathrm{O}_2)_2\mathrm{Pbo}'' &= \mathbf{Pb}\mathrm{O} + \mathrm{O} + \mathbf{N}_2\mathrm{O}_4 \; \text{(Exp. 66).}
\end{aligned}$$

Resolution is often accompanied by **combination** in the presence of an element or a compound body, which exerts an affinity for one of the elements, *e.g.*,

$$\begin{aligned}
\mathrm{Cu} + \mathbf{N}_2\mathrm{O}_5 &= \mathbf{N}_2\mathrm{O}_4 + \mathbf{Cu}\mathrm{O} \; \text{(Exp. 67).}\\
\mathrm{Cu} + \mathbf{S}\mathrm{O}_3 &= \mathbf{S}\mathrm{O}_2 + \mathbf{Cu}\mathrm{O} \; \text{(Exp. 64).}
\end{aligned}$$

III. When an element or group of elements in a body is displaced by another element or group of elements.

This change comprises many interesting reactions based upon the displacement of a less electropositive by a more electropositive element: *e.g.*,

$$2\mathbf{O}H_2 + Na_2 = H_2 + 2NaHo \text{ (Exp. 1).}$$

Iron displacing copper in copper salts:—

$$\mathbf{S}O_3Cuo'' + Fe = \mathbf{S}O_2Feo'' + Cu.^{*}$$

Zinc or copper displacing silver in silver salts:—

$$2AgCl + Zn = \mathbf{Zn}Cl_2 + Ag_2.$$

The more electropositive metal displacing, in fact, the less electropositive in the following order:—

Zn, Fe, Cu, Sn, Pb, Hg, Ag, Pt, Au.

In the dry way, the more electropositive metal sodium, when heated with dry aluminic chloride, $\mathbf{Al}^{iv}{}_2Cl_6$, yields aluminium and sodic chloride:—

$$\mathbf{Al}_2Cl_6 + 3Na_2 = 2Al + 6NaCl.$$

Magnesic iodide, when heated with sodium, yields magnesium:—

$$\mathbf{Mg}I_2 + Na_2 = Mg + 2NaI.$$

Hydrogen, carbon or carbonic oxide, set free the metal in metallic oxides, *e.g.*:—

$$\begin{aligned} \mathbf{O}Na_2 &+ C &= Na_2 &+ \mathbf{C}''O \text{ (Exp. 28).}\\ \mathbf{Cu}O &+ H_2 &= Cu &+ \mathbf{O}H_2 \text{ (Exp. 27).}\\ 2\mathbf{Pb}O &+ C &= 2Pb &+ \mathbf{C}^{iv}O_2 \text{ (Exp. 87).} \end{aligned}$$

A change of this kind is usually termed a **reduction.** Hydrogen displaces metals from most oxides only at a high temperature. It is without action upon the oxides of potassium, sodium, barium, strontium, calcium, aluminium. The oxides of mercury, silver, platinum, and gold are reduced by hydrogen at a temperature a little above 100° C.; whilst the other oxides are for the most part only reduced at a red heat.

The oxides of iron are reduced to metallic iron by hydrogen with formation of steam; and yet one of the methods for preparing hydrogen consists in passing steam over iron-turnings, placed in a gun barrel and heated in a furnace. This curious *reciprocal* action depends evidently upon the relative quantities of iron oxide and hydrogen, and of metallic iron and steam, which are acted upon. In the one case the steam formed by the reduction of the ferric oxide in a current of hydrogen is immediately carried along by the excess of hydrogen gas and removed out of contact with the reduced metal; in the second the steam is largely in excess and carries along the liberated hydrogen. Temperature likewise influences these changes.

In carbon we possess a most powerful reducing agent. It reduces not only all oxides which are decomposed by hydrogen, but likewise, at a white heat, oxides which are not reduced by hydrogen, *e.g.*, $\mathbf{O}K_2, \mathbf{O}Na_2$ (Exp. 28).

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[*] Some illustrations of chemical changes are used in this chapter with which the student has not yet become acquainted. They will be explained in the second part of the book.

An element or group of elements, can displace another element or group of elements, with formation of salts; as when an acid is made to act upon different metals, *e.g.*:—

$$2HCl + Zn = H_2 + \mathbf{Zn}Cl_2 \text{ (Exp. 2).}$$
$$\mathbf{S}O_2Ho_2 + Fe = H_2 + \mathbf{S}O_2Feo'' \text{ (Exp. 2).}$$

or when silicic anhydride is fused with potassic carbonate or nitre:—

$$\mathbf{C}OKo_2 + \mathbf{Si}O_2 = \mathbf{Si}OKo_2 + \mathbf{C}O_2 \text{ (Exp. 92).}$$
$$2\mathbf{N}O_2Ko + \mathbf{Si}O_2 = \mathbf{Si}OKo_2 + \mathbf{N}_2O_4 + O \text{ (Exp. 93).}$$

The more volatile acid, as a rule, is driven out or displaced by the less volatile body, *e.g.*:—

$$\mathbf{S}O_2Ko_2 + \mathbf{B}_2O_3 = \mathbf{S}O_3 + 2\mathbf{B}OKo \text{ (Chap. xvii).}$$

By far the most important are the chemical changes which are produced.

Matter undergoes, lastly, a chemical change—

IV. When a mutual exchange of elements or groups of elements in two or more bodies takes place.

These are often designated changes by **double decomposition**. A great number of chemical bodies originate in an exchange of this kind.

It enables us, for instance, to convert—

a. Chlorides into hydrates, by the action of water or alkaline hydrates, *e.g.*:—

$$\mathbf{P}Cl_3 + 3\mathbf{O}H_2 = \mathbf{P}OHHo_2 + 3HCl.$$

Phosphorous trichloride. Phosphorous acid.

$$\mathbf{Cu}Cl_2 + 2NaHo = \mathbf{Cu}Ho_2 + 2NaCl.$$

b. Oxides or hydrates into chlorides, by the action of hydrochloric acid, *e.g.*:—

$$\mathbf{Cu}O + 2HCl = \mathbf{Cu}Cl_2 + \mathbf{O}H_2 \text{ (Exp. 57).}$$
$$NaHo + HCl = NaCl + \mathbf{O}H_2 \text{ (Exp. 59).}$$

c. Sulphides into oxides, by the action of water (steam), *e.g.*:—

$$\mathbf{Fe}S + \mathbf{O}H_2 = \mathbf{Fe}O + \mathbf{S}H_2.$$

d. Oxides or hydrates into sulphides, by means of sulphuretted hydrogen, *e.g.*:—

$$\mathbf{Pb}O + \mathbf{S}H_2 = \mathbf{Pb}S + \mathbf{O}H_2 \text{ (Exp. 43).}$$
$$\mathbf{Fe}Ho_2 + \mathbf{S}H_2 = \mathbf{Fe}S + 2\mathbf{O}H_2 \text{ (Exp. 43).}$$

e. Sulphides into Chlorides, by means of hydrochloric acid, *e.g.*:—

$$\mathbf{Zn}S + 2HCl = \mathbf{Zn}Cl_2 + \mathbf{S}H_2 \text{ (Exp. 42).}$$

f. Chlorides into Sulphides, by the action of sulphuretted hydrogen, *e.g.*:—

$$\mathbf{Hg}Cl_2 + \mathbf{S}H_2 = \mathbf{Hg}S + 2HCl \text{ (Exp. 43).}$$

On adding an acid to a solution of a salt, a mutual exchange takes place, which is frequently imperceptible to the eye, or is indicated only by a change in the colour of the liquid.

a. A solution of $\mathbf{N}O_2Ko$, when treated with dilute $\mathbf{S}O_2Ho_2$, shows no signs of decomposition; but on evaporation, $\mathbf{S}O_2Ko_2$ crystallises out, it being less soluble than $\mathbf{N}O_2Ko$. Nitric acid, on the other hand, is capable of decomposing potassic sulphate, provided the evaporation be conducted at a sufficiently low temperature (0° C.), at which $\mathbf{N}O_2Ko$ is less soluble than $\mathbf{S}O_2Ko_2$.

On adding a solution of hydrochloric acid to a solution of cupric sulphate, the partial exchange expressed by the equation—

$$\mathbf{S}O_2Cuo'' + 2HCl = \mathbf{Cu}Cl_2 + \mathbf{S}O_2Ho_2,$$

is merely marked by a change of colour, from light blue (the colour of a solution of $\mathbf{S}O_2Cuo''$), to green (the colour of $\mathbf{Cu}Cl_2$).

b. The acid which is added forms with the base of certain salts a scarcely soluble compound, which is not precipitated from a dilute solution, *e.g.*:—

$$(\mathbf{N}O_2)_2Pbo'' + 2HCl = \underset{\substack{\text{Soluble in}\\ \text{much water.}}}{\mathbf{Pb}Cl_2} + 2\mathbf{N}O_2Ho.$$

c. A *volatile acid* (or anhydride) is evolved, either at the ordinary temperature or on the application of heat, *e.g.*:—

$$\begin{array}{llllll}
NaCl & + \mathbf{S}O_2Ho_2 & = HCl & + \mathbf{S}O_2HoNao & \text{(Exp. 56).} \\
\mathbf{N}O_2Nao & + \mathbf{S}O_2Ho_2 & = \mathbf{N}O_2Ho & + \mathbf{S}O_2HoNao & \text{(Exp. 65).} \\
3\mathbf{S}O_2Nao_2 & + 2\mathbf{P}OHo_3 & = 3\mathbf{S}O_2Ho_2 & + 2\mathbf{P}ONao_3 & \text{(Chap. xvi).} \\
\mathbf{C}OCao'' & + 2HCl & = \mathbf{C}O_2 & + \mathbf{Ca}Cl_2 + \mathbf{O}H_2 & \text{(Exp. 61).} \\
\mathbf{Ca}F_2 & + \mathbf{S}O_2Ho_2 & = 2HF & + \mathbf{S}O_2Cao''. & \\
\mathbf{S}ONao_2 & + \mathbf{S}O_2Ho_2 & = \mathbf{S}O_2 & + \mathbf{S}O_2Nao_2 + \mathbf{O}H_2 & \text{(Chap. xiii).}
\end{array}$$

d. The *acid* is liberated from the salt and is nearly *insoluble* in water (no change may possibly be observed in dilute solutions), *e.g.*:—

$$\begin{array}{lllll}
\mathbf{Si}ONao_2 & + 2HCl & + \mathbf{O}H_2 & = \mathbf{Si}Ho_4 & + 2NaCl \text{ (Exp. 91).} \\
\mathbf{Si}ONao_2 & + \mathbf{S}O_2Ho_2 & + \mathbf{O}H_2 & = \mathbf{Si}Ho_4 & + \mathbf{S}O_2Nao_2. \\
\mathbf{B}_4O_5Nao_2 & + 2HCl & + \mathbf{O}H_2 & = 4\mathbf{B}OHo & + 2NaCl \text{ (Exp. 85).}
\end{array}$$

e. A *precipitate* is produced, owing to the insolubility of one of the groups of elements (produced by a mutual exchange between salt and acid), *e.g.*:—

$$\mathbf{Ba}Cl_2 + \mathbf{S}O_2Ho_2 = \underset{\substack{\text{Insoluble in}\\ \text{water and}\\ \text{acids.}}}{\mathbf{S}O_2Bao''} + 2HCl.$$

$$\begin{array}{llll}
\mathbf{N}O_2Ago & + HCl & = AgCl & + \mathbf{N}O_2Ho. \\
\mathbf{S}O_2Ago_2 & + 2HCl & = 2AgCl & + \mathbf{S}O_2Ho_2. \\
(\mathbf{N}O_2)_2Pbo'' & + \mathbf{S}O_2Ho_2 & = \mathbf{S}O_2Pbo'' & + 2\mathbf{N}O_2Ho.
\end{array}$$

A similar exchange of elements frequently takes place when a solution of one salt is added to a solution of another salt, *e.g.*:—

$$\begin{array}{llll}
\mathbf{Ba}Cl_2 & + \mathbf{S}O_2Ko_2 & = \mathbf{S}O_2Bao'' & + 2KCl. \\
\mathbf{N}O_2Ago & + NaCl & = AgCl & + \mathbf{N}O_2Nao. \\
(\mathbf{N}O_2)_2Pbo'' & + \mathbf{C}ONao_2 & = \mathbf{C}OPbo'' & + 2\mathbf{N}O_2Nao. \\
\mathbf{S}O_2Bao'' & + \mathbf{C}ONao_2 & = \mathbf{C}OBao''^{*} & + \mathbf{S}O_2Nao_2.
\end{array}$$

The mutual exchange of elements between two salts need not necessarily be accompanied by the precipitation of a group of elements; it frequently suffices if the new compound be rendered less soluble than either of the two salts which were mixed together, *e.g.*,

A solution of KCl and $\mathbf{N}O_2Nao$ when evaporated at a low temperature, yields the two salts unchanged; KCl crystallises out first. But on boiling the

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[*] By fusion with fusion-mixture, or by long-continued boiling with alkaline carbonates.

solution of the two salts, NaCl crystallises out, and $\mathbf{N}O_2Ko$ remains in solution, being more soluble than NaCl (comp. Chap. xx). On drawing off the boiling solution from the crystallised NaCl, potassic nitrate crystallises out on cooling.

Then, again, on mixing solutions of NaCl and $\mathbf{S}O_2Mgo''$, it is impossible to say how the acids and bases remain combined. They may exist

1st, as NaCl and $\mathbf{S}O_2Mgo''$,
2nd, as $\mathbf{Mg}Cl_2$ and $\mathbf{S}O_2Nao_2$,
3rd, as NaCl, $\mathbf{Mg}Cl_2$, $\mathbf{S}O_2Nao_2$, $\mathbf{S}O_2Mgo''$;

but on evaporating the solution above 15° C., NaCl crystallises out first (being the least soluble of the above salts at this temperature), and $\mathbf{S}O_2Mgo''$ next, mixed with a little NaCl. When evaporated at a lower temperature, *e.g.*, at 0° C., $\mathbf{S}O_2Nao_2$ (being the least soluble at this low temperature) crystallises out first, and leaves $\mathbf{Mg}Cl_2$ in solution.

Heat promotes the exchange of elements between two salts of different acids and bases: *e.g.*,

$$2AmCl + \mathbf{C}OCao'' = \mathbf{Ca}Cl_2 + \mathbf{C}OAmo_2.$$

The change is owing to the volatile nature of ammonic carbonate,

$$\mathbf{S}O_2Ko_2 + 2AmCl = \mathbf{S}O_2Amo_2 + 2KCl.$$

These decompositions are frequently the reverse of the reactions which take place in the cold, between the solutions of two salts, *e.g.*,

$$\mathbf{Ca}Cl_2 + \mathbf{C}OAmo_2 = \mathbf{C}OCao'' + 2AmCl.$$

owing to the insolubility of the calcic carbonate.

Heat promotes likewise the formation of double silicates and borates, fluorides and chlorides. These compounds are frequently broken up again on being dissolved in water, the original salts being produced.

For purposes of reference, the four different changes just enumerated may be indicated by employing the bracketed letters—

(C) standing for Change I, *i.e.*, **Combination.**
(R) „ „ II, *i.e.*, **Resolution.**
(D) „ „ III, *i.e.*, **Displacement.**
(DD) „ „ IV, *i.e.*, **Double Decomposition.**

PART II.

A COURSE OF QUALITATIVE CHEMICAL ANALYSIS.

CHAPTER I.

DEFINITION OF QUALITATIVE ANALYSIS.—REAGENTS.—CHEMICAL OPERATIONS.—GROUP-REAGENTS AND SPECIAL REAGENTS.

CHEMICAL analysis consists in the performance of certain experiments:—with the object of putting, so to speak, certain questions to a substance, in order to ascertain the presence or absence of certain bodies. It is termed *qualitative* analysis, if the answer which is received reveals merely *what kind* of matter is present (from *qualis*), without regard to quantity. It is essential that these questions should not be put at random, but according to a well-considered, systematic order; and that the answers should be interpreted correctly.

We have already seen, that there exists a resemblance between certain elementary as well as certain compound bodies; at the same time the metallic, like the non-metallic elements, bear the stamp of a marked individuality which renders every classification, from whatever point of view we attempt it, more or less difficult—a difficulty which extends likewise to the various compounds which the elements form. Thus silver, which is classified (page 60) with the monad metals potassium and sodium, differs in a marked manner from the alkali metals. Iron, which exists in the dyad form in $\mathbf{Fe}Cl_2$ (ferrous chloride), and in the tetrad condition in $\left\{\begin{array}{l}\mathbf{Fe}Cl_3\\ \mathbf{Fe}Cl_3\end{array}\right.$ (ferric chloride), partakes in the dyad form of the character of the isomorphous diatomic metals of the magnesium group, *e.g.*, manganese and zinc; and resembles in the tetrad form aluminium and chromium. Copper, which in its cupric compounds offers certain points of resemblance to the magnesium group, resembles also in many respects the metals of the mercury group;* the general composition of the cuprous and mercurous and the cupric and mercuric oxides and chlorides being the same. Inorganic (as well as organic) compound bodies bear, for the most part, the impress of the elementary bodies which enter into their composition; and compounds built up of elements which have equal numbers of bonds, frequently show a certain analogy in their structure as well as a considerable similarity in their reactions. In studying the chemical changes to which the various bodies—elementary or compound—can be submitted, our attention must be mainly directed towards discovering and defining this similarity and dissimilarity.

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* H. Wurtz, Leçons de Philosophie chimique, p. 170.

We employ *reagents*[*] as the means of producing chemical changes. By reagents are meant bodies—either elementary or compound—which are capable of *reacting* upon and revealing to us the nature of the substances under examination. They are usually divided, without any strict line of demarcation, into two classes; viz., *general* and *special reagents*. General reagents are those which separate a number of substances—groups in fact—at one operation; and special reagents those which are used to a limited extent only, and for the detection of *individual* substances.

In a laboratory the general reagents are most conveniently arranged over the working table within reach of each operator; whilst the special reagents intended for the use of a number of chemical students, are usually placed in a freely accessible part of the laboratory.

A list of reagents, as well as directions for their preparation, will be found in the Appendix. Chemical students who have not the advantage of working in a well appointed laboratory, should devote much attention and care to the preparation of the reagents.

Chemical Operations.—We add a **reagent** to a solution of an unknown body either by pouring it directly from the bottle, or by running it from a pipette, as shown in Fig. 70, with the view of producing a **precipitate**;[†] *i.e.*, of converting the body from the soluble to the insoluble state. The reaction which takes place is mostly *a change by double decomposition*. Sometimes a precipitation is produced by voltaic action, sometimes merely by the substitution of one solvent for another. One or more bodies may be precipitated by one and the same reagent. As most precipitates are heavier than the liquid in which they are suspended, they fall to the bottom with more or less rapidity; and the supernatant liquid may often be poured off or **decanted**, without much disturbing the precipitate. This mode of separating fluids from precipitates is by far the most expeditious, and should be resorted to whenever it is applicable. The precipitate may be washed in the vessel itself by treatment with hot water and repeated decantation.

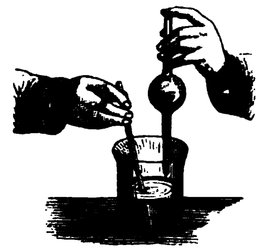

FIG. 70.

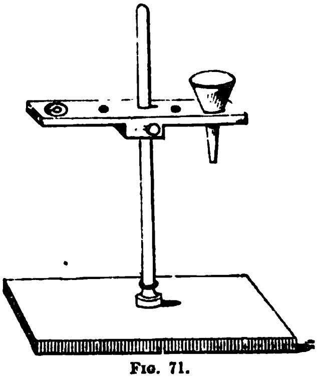

FIG. 71.

When a large quantity of a fluid has to be removed from a precipitate, it is best to **siphon** off the supernatant fluid. The precipitate may be washed with water, and the wash-water siphoned off repeatedly.

Small quantities of a precipitate which do not subside readily are more quickly separated by **filtration**. For this purpose **funnels** are used, mostly of glass, conical in shape, and inclined at an angle of 60°. They may be conveniently supported on a wooden stand, Fig. 71, or an iron or brass

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[*] Comp. Chapter III, Part I.

[†] Comp. Chapter VII, Part I.

filtering stand as seen in Fig. 72. The **filtering paper** should be porous and unsized, and cut in the form of a round sheet, which by being folded twice in the shape of a quadrant, forms, on opening up, a paper cone, at an angle of 60°. The **filter** should exactly fit the funnel, without reaching quite to the rim, and should be moistened in the funnel with distilled water before any liquid is poured through it. As most kinds of filtering paper contain traces of iron, lime, silica, etc.,—with the exception of the so-called Swedish filtering paper, which contains scarcely perceptible traces of mineral substances,—acid liquids frequently dissolve out traces of these bodies. In all accurate analyses the filtering paper should, on this account, be washed first with dilute hydrochloric or nitric acid, and then with hot water, before being used; or else Swedish filter paper only should be employed.

Most precipitates retain with great pertinacity traces of the fluid in which they were suspended, and it is therefore of the utmost importance to thoroughly wash them, in order to obtain accurate results. For this purpose a **wash-bottle** (Fig. 72) is employed, whereby a fine jet of hot or cold distilled water can be directed on to the filter in such a manner as to loosen and detach the precipitate from the paper. The liquid should at no time quite fill the filter, as some precipitates have a tendency to creep up and to get between the paper and the glass, and are carried into the **filtrate.** This would entail repeated filtration. The washing of a precipitate on the filter is effected most rapidly by allowing the wash-water to run off entirely each time before adding fresh quantities of distilled water. By repeating this four or five times, most precipitates will be found sufficiently washed for qualitative purposes.

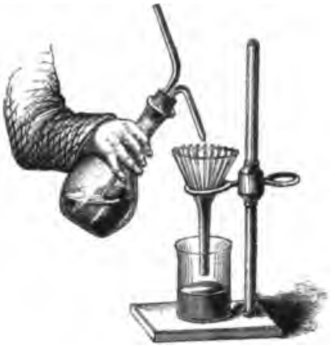

FIG. 72.

The student should guard himself against using too large a quantity of the substance which he wishes to examine. Heavy precipitates entail much washing, an operation which is most tedious and yet indispensable.

Test tubes answer the purposes of precipitation and separation in qualitative analysis, especially as there is generally no need for collecting the wash-water or adding it to the main filtrate. These tubes are conveniently placed in a **test-tube stand** (Fig. 73). After being well cleansed by the aid of a test-tube

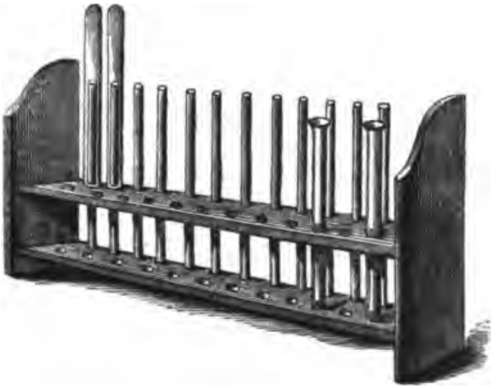

FIG. 73

brush, and rinsed out with distilled water, they should be set aside to drain in a basket.

Beakers are sometimes employed if an analysis involves the separation of a small quantity of one substance from a large amount of another, and when, of necessity, large quantities of the substance must be operated upon.

Porcelain dishes are employed for the purpose of concentration, or evaporation and ignition. They can be heated either by means of a **spirit lamp** (Fig. 74), or a so-called **Berzelius lamp** (Fig. 75), or, where coal gas can be procured, by means of a **Bunsen gas lamp**, provided with a rose top, as was shown in Fig. 12. Sometimes a sheet of iron wire gauze or a sand-bath is interposed between the porcelain vessel and the gas flame, and is supported on a retort ring or tripod stand. A convenient tripod support for porcelain and glass vessels is shown in Figs. 30 and 41, which prevents at the same time the flame from being blown about.

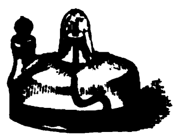

FIG. 74.

If solid substances have to be examined, they should always be **powdered** in a **mortar**—an agate mortar should be employed for hard substances, such as minerals—before being dissolved in water, acids, etc.

Reactions involving the use of valuable reagents—such as salts of gold, platinum, silver—should be performed on **watch-glasses**, with small quantities of the substance only.

For the **ignition** of precipitates we employ mostly porcelain crucibles, or small porcelain dishes.

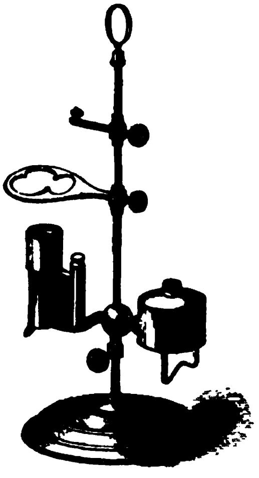

FIG. 75.

A knowledge of qualitative analysis enables us—

1. *To recognize with speed and certainty the presence of various elementary and compound bodies.*
2. *To effect their separation from each other.*

In order to accomplish this we shall study more particularly those chemical reactions—both in the dry and in the wet way—which are essential; but shall endeavour, at the same time, to give as complete a view as possible of other chemical changes which serve the purposes of qualitative analysis, and which on this and other grounds possess considerable interest.

We shall confine ourselves to the study of the 36 most important elements and their compounds.

There are certain reagents which effect the separation of a number of bodies contained in a common solution leaving all the others in solution. Such general reagents are then called *group-reagents*.

Dissolve in water small quantities of
Argentic nitrate*

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[*] Solutions of salts of the different metals containing five milligrammes of the metal in a cubic centimetre are conveniently prepared and kept for use.

Cupric nitrate.
Cobaltic "
Baric "
Potassic "

To the solution add—

HCl, a *white curdy* precipitate is obtained, which consists of **argentic chloride**, $AgCl$; filter. To the filtrate add—

$\mathbf{S}H_2$, a *black* precipitate is obtained consisting of **cupric sulphide**, $\mathbf{Cu}S$; filter again, and to the filtrate add—

$AmCl$, $AmHo$, and $\mathbf{S}Am_2$ } A *black* precipitate comes down consisting of **cobaltous sulphide**, $\mathbf{Co}S$; filter, and to the filtrate add—

$\mathbf{C}OAmo_2$, a white precipitate is obtained, consisting of **baric carbonate**, $\mathbf{C}OBao''$; filter, evaporate the filtrate and ignite to drive off the ammonic salts. A white saline residue is left, containing **potassic nitrate**.

What were the chemical changes that took place?

The changes were evidently produced *by the mutual exchange of elements in two bodies* (changes by *double decomposition*): *i.e.*, the hydrochloric acid added in Group I. to the solution of the metallic nitrates, exchanged its hydrogen for the silver of the argentic nitrate; and the sulphuretted hydrogen exchanged its hydrogen for the metal copper, leaving nitric acid and cupric sulphide, etc.

The reactions may be expressed by the following equations:—

$\mathbf{N}O_2Ago$ Argentic nitrate.	+	HCl	=	$AgCl$ Argentic chloride.	+	$\mathbf{N}O_2Ho$.
$\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Cuo''$ Cupric nitrate.	+	$\mathbf{S}H_2$	=	$\mathbf{Cu}S$* Cupric sulphide.	+	$2\mathbf{N}O_2Ho$.
$\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Coo''$ Cobaltous nitrate.	+	$\mathbf{S}Am_2$	=	$\mathbf{Co}S$ Cobaltous sulphide.	+	$2\mathbf{N}O_2Amo$.
$\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Bao''$ Baric nitrate.	+	$\mathbf{C}OAmo_2$	=	$\mathbf{C}OBao''$ Baric carbonate.	+	$2\mathbf{N}O_2Amo$.

Silver, copper, cobalt, and potassium are, however, not the only metals which might have been separated by these same reagents.

The following table exhibits the five groups into which all metallic bodies classify themselves on the addition of the several group-reagents.

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* It is immaterial whether we write $\mathbf{S}Cu$ or $\mathbf{Cu}S$, since both sulphur and copper are dyad elements.

ANALYTICAL CLASSIFICATION OF THE METALS,

WITH THEIR RESPECTIVE GROUP-REAGENTS.

GROUP I. Hydrochloric Acid.	GROUP II. Sulphuretted Hydrogen in acid solutions.	GROUP III. Ammonic chloride, Ammonia, and Ammonic Sulphide.	GROUP IV. Ammonic Chloride, Ammonia, and Ammonic Carbonate.	GROUP V. (No Group reagent.)
Lead .... as $\mathbf{Pb}\mathrm{Cl}_2$.*	Mercury...... as $\mathbf{Hg}\mathrm{S}$, *black.*	(1.) **Hydrates.**	Barium as $\mathbf{C}\mathrm{OBao}''$.	**In Solution:**
Silver.... „ AgCl.	Lead .... „ $\mathbf{Pb}\mathrm{S}$,‡ „	Aluminium .. as $\mathbf{Al}_2\mathrm{Ho}_6$.	Strontium „ $\mathbf{C}\mathrm{OSro}''$.	Magnesium.
Mercury „ $\mathbf{Hg}_2\mathrm{Cl}_2$.†	Bismuth .... „ $\mathbf{Bi}_2\mathrm{S}_3$, „	Chromium .. „ $\mathbf{Cr}_2\mathrm{Ho}_6$, *green.*	Calcium „ $\mathbf{C}\mathrm{OCao}''$.	Potassium.
	Copper ...... „ $\mathbf{Cu}\mathrm{S}$ „	(2.) **Sulphides.**		Sodium.
	Cadmium .... „ $\mathbf{Cd}\mathrm{S}$, *yellow.*	Iron .... as $\mathbf{Fe}\mathrm{S}$, *black.*		Ammonium.
	Tin (Stannosum) „ $\mathbf{Sn}\mathrm{S}$, *black.*	Zinc .... „ $\mathbf{Zn}\mathrm{S}$, *white.*		
	„ (Stannicum) „ $\mathbf{Sn}\mathrm{S}_2$, *yellow.*	Manganese .. „ $\mathbf{Mn}\mathrm{S}$, *buff.*		
	Antimony .... „ $\mathbf{Sb}_2\mathrm{S}_3$, *orange.*	Nickel ...... „ $\mathbf{Ni}\mathrm{S}$, *black.*		
	Arsenic ...... „ $\mathbf{As}_2\mathrm{S}_3$, *yellow.*	Cobalt ...... „ $\mathbf{Co}\mathrm{S}$, „		
	Gold .... „ $\mathbf{Au}_2\mathrm{S}_3$, *black.*	(3.) **Certain Salts,**		
	Platinum .... „ $\mathbf{Pt}\mathrm{S}_2$, „	such as alkaline earthy phosphates, &c., &c.		

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* When no colour is stated, the precipitate is *white.*

† Precipitated as mercurous chloride from mercurous salts.

‡ Lead being somewhat soluble in water in the form of plumbic chloride, $\mathbf{Pb}\mathrm{Cl}_2$, occurs in the first and second groups.

Thus far *group*-reagents assist us in separating bodies, but when, as in Group IV, the white precipitate produced by the group-reagent, $\mathrm{COAmo_2}$, leaves us still in doubt whether a barium, strondium, or calcium compound was present in the solution, further experiments must evidently be made with a view of completely identifying the substance under examination. This the student will only be able to do by making himself first practically familiar with the different changes or reactions which the members of the various groups of metals can be made to undergo: and after understanding the use of the group-reagents, he should direct his attention to the special reactions *which distinguish and separate one metal from another or from several others.* This may frequently be done in more than one way; one reaction, however, as a rule, deserves the preference over others, on account of the greater exactness which distinguishes it, or on account of increased facility of execution, or of both.

Certain reactions, lastly, will have to be studied, which are not directly available for the separation of the members of a group from each other, but to which considerable interest is attached as being illustrative of some valuable property or other of the metals.

The tabular form, which is, no doubt, the most compact and summary mode of arranging chemical reactions, will often be adopted for embodying such reliable and expeditious methods of separation as have stood the test of experience in the laboratory. The directions given will be concise and divested of all explanatory matter. On no account should a student use any tabular directions, however, without first having made himself practically acquainted with the details of the reactions; and to counteract any pernicous influence which the use of tables might have, the student should learn to draw up tables for the several other processes of separation which are frequently possible.

A deviation from the natural course of studying the reactions of the metals by beginning with Group I, and so on, will be justified on the ground of greater simplicity, and on account of the far greater importance which is attached to the metals of Group V, especially the alkali metals. Experience has shown that students have less difficulty in mastering the reactions by reversing the order of the groups, beginning with the study of the alkali and alkaline-earthy metals; and that a thorough knowledge of the metals of these groups is of material assistance in understanding the qualitative changes to which the metals proper are subjected.

CHAPTER II.

REACTIONS OF THE METALS OF GROUP V.

THIS group comprises the metals POTASSIUM, SODIUM, AMMONIUM, and MAGNESIUM, which are not precipitated by any group-reagent.

1. **POTASSIUM,** K.—Occurs in nature only in a few minerals, of which *nitre* or *saltpetre* is the most important. Potassium is present in larger or smaller quantities in a few silicates and sulphates, such as *felspar*, *alumstone*. It is also found in the ashes of plants (*crude potashes*), and in the form of chloride in saline deposits (at Stassfurth, in Prussia, and elsewhere).

REACTIONS IN THE DRY WAY.

Potassium compounds, when heated on platinum wire in the inner flame of the blowpipe impart a **violet colour** to the outer flame.

This applies more particularly to potassic salts which are volatile without decomposition at a very strong heat (such as potassic chloride, bromide, and iodide) or which are decomposed by heat; but not to non-volatile potassic salts, such as phosphates or borates, which give scarcely any flame reaction. The presence of sodium compounds gives rise to an intense *golden yellow* flame, and conceals the potassium reaction; but when seen through a blue **glass**, or indigo-prism, the yellow or sodium flame is entirely cut off, and the potassium flame becomes distinctly visible, and is then of a *rich reddish-violet* colour.

REACTIONS IN THE WET WAY.

WE EMPLOY A SOLUTION OF POTASSIC CHLORIDE, KCl.

$\mathbf{Pt}Cl_4$ (**platinic chloride**) precipitates from potassic solutions which are not too dilute, a *yellow crystalline* precipitate of **potassic platinic chloride,** $2KCl, \mathbf{Pt}Cl_4$, insoluble* in alcohol and ether, as well as in acids.

$\left\{\begin{array}{l}\mathbf{C}\mathrm{OHo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{OHo}\end{array}\right.$ (**Tartaric acid**) precipitates *white crystalline* **hydric potassic Tartrate,** $\left\{\begin{array}{l}\mathbf{C}\mathrm{OKo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{OHo}\end{array}\right.$, from neutral and sufficiently concentrated solutions. The precipitate settles rapidly, especially on shaking or stirring.

$2HF, \mathbf{Si}F_4$ (**hydrofluosilicic acid**) gives a *white gelatinous* precipitate of **potassic silicofluoride,** $2KF, \mathbf{Si}F_4$.

Potassic salts are for the most part soluble in water, hence so few reactions; the hydrate and carbonate constitute two important reagents, on account of the great affinity which the powerful base potassa possesses for the acids with which the metals of other groups may be combined.

2. **SODIUM,** Na.—Occurs in nature in vast masses, as *rock salt*, NaCl; as CARBONATE, in *native soda*, $\mathbf{C}\mathrm{ONao_2}, 10\mathbf{O}H_2$, and in *trona*, $\mathbf{C}\mathrm{ONao_2}, 2\mathbf{C}\mathrm{OHoNao}, 3\mathbf{O}H_2$; as NITRATE, in *cubic nitre*, or *Chili saltpetre*, $\mathbf{N}\mathrm{O_2Nao}$; as SULPHATE or *glauber salt*, $\mathbf{S}\mathrm{O_2Nao_2}, 10\mathbf{O}H_2$; as *biborate*, $\mathbf{B}_4\mathrm{O_5Nao_2}, 10\mathbf{O}H_2$; as *glauberite*, $\begin{matrix}\mathbf{S}\mathrm{O_2}\\ \mathbf{S}\mathrm{O_2}\end{matrix}\mathrm{Ko_2Cao''}$, and as *cryolite*, $6NaF, \mathbf{Al}_2F_6$, and in many SILICATES, of which *albite* may be taken

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* The degree of solubility of a precipitate in different media can only be ascertained by laborious *quantitative* experiments. The student will therefore be expected to verify only those statements respecting the solubility of the precipitates which require no quantitative knowledge.

as the representative. All natural sodium compounds, with the exception of the last two minerals are soluble in water.

REACTIONS IN THE DRY WAY.

We almost exclusively rely for the detection of sodium upon the characteristic colour—an intense **golden yellow**—which its compounds impart to the outer flame of the blowpipe. Some sodic salts are readily recognized by their characteristic taste, especially rock salt and cubic nitre.

REACTIONS IN THE WET WAY.

We employ a SOLUTION OF SODIC CHLORIDE, $NaCl$.

Sodic salts are even more freely soluble than potassic salts, and platinic chloride or tartaric acid give no precipitates. Hydrofluosilicic acid gives a gelatinous precipitate from concentrated solutions only.

SbO_2Ko (**potassic metantimoniate**) produces a *white crystalline* precipitate of **sodic metantimoniate**, from neutral or alkaline solutions, if they are not too dilute. The precipitate is insoluble in alcohol. (The solution should only contain alkali metals.)

Sodic hydrate and sodic carbonate act in every respect like potassic hydrate or carbonate. Pure sodic hydrate is now prepared from the metal sodium, and deserves the preference over potassic hydrate.*

3. AMMONIUM.—Am = NH_4 (comp. Chap. XV, Part I).

REACTIONS IN THE DRY WAY.

Ammonic salts, when heated in a test-tube, **volatilize**, either entirely or partially. Salts with fixed acids, such as phosphoric acid, lose ammonia, NH_3. Salts of ammonium with volatile acids can be volatilized, either with decomposition, such as the nitrate, nitrite, sulphate; or without decomposition, such as the chloride, bromide, iodide: the latter salts condense again unchanged; they *sublime*, and are found in the upper part of the test tube.

REACTIONS IN THE WET WAY.

We employ a SOLUTION OF AMMONIC CHLORIDE, $AmCl$.

$PtCl_4$ produces a *heavy yellow* precipitate of **ammonic platinic chloride**, $2AmCl$, **$PtCl_4$**. The precipitate is soluble in much water (hence there appears no precipitate from dilute ammonic solutions); but insoluble in alcohol and ether. Ammonic platinic chloride leaves on ignition only spongy platinum. (DISTINCTION FROM POTASSIC PLATINIC CHLORIDE, which leaves spongy platinum and potassic chloride, $Pt + 2KCl$).

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* The student should make himself quite familiar with the properties of the various salts of potassium and sodium, also with the interesting processes of manufacturing sodic carbonate from the chloride; sodic silicate (*water-glass*); potassic chlorate, &c., &c.

$\left\{\begin{array}{l}\mathbf{C}\mathrm{OHo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{OHo}\end{array}\right.$ (**tartaric acid**) produces from a concentrated solution of ammonic chloride a *white crystalline* precipitate of **hydric ammonic tartrate**, resembling the potassium precipitate in its properties. The two precipitates are readily distinguished on ignition. Hydric potassic tartrate leaves a carbonaceous residue, which is strongly alkaline, and dissolves in water (potassic carbonate); the other leaves merely a residue of carbon, devoid of any alkaline reaction.

Ammonic salts are decomposed with evolution of ammonia gas when heated with a hydrate of an alkali (KHo,NaHo), or alkaline earthy metal ($\mathbf{Ba}\mathrm{Ho}_2$,$\mathbf{Ca}\mathrm{Ho}_2$), thus:—

$$2\mathrm{AmCl} + \mathbf{Ca}\mathrm{Ho}_2 = 2\mathbf{N}\mathrm{H}_3 + \mathbf{Ca}\mathrm{Cl}_2 + 2\mathbf{O}\mathrm{H}_2.$$

Ammonia gas is readily recognized, 1st, by *its pungent odour;* 2nd, by *its turning red litmus paper*, moistened with a drop of distilled water, *blue;* 3rd, by *its combining with the vapour of volatile acids* (such as hydrochloric acid), to form white fumes (AmCl).

Nessler's test* for *traces* of ammonia.—If a potassic solution of potassic mercuric iodide, 2KI, $\mathbf{Hg}\mathrm{I}_2$, be added to a fluid containing mere traces of ammonia or of an ammonic salt, a *brown* precipitate of dimercurammonic iodide or *yellow to brown coloration* is produced, according to the quantity of the ammonium compound present—

$$2(2\mathrm{KI},\mathbf{Hg}\mathrm{I}_2) + 3\mathrm{KHo} + \mathbf{N}\mathrm{H}_4\mathrm{Ho} = \underset{\text{Brown pp.}}{\mathbf{N}\mathrm{Hg}''_2\mathrm{I},\mathbf{O}\mathrm{H}_2} + 7\mathrm{KI} + 3\mathbf{O}\mathrm{H}_2.$$

Ammonic hydrate and carbonate, as well as various other ammonium compounds, *e.g.*, ammonic chloride, are among the most useful reagents which we possess.

QUESTIONS AND EXERCISES.

1. Mention some natural compounds in which potassium occurs.
2. How are potassium compounds recognized in the wet way?
3. How can potassium and sodium compounds be distinguished before the blowpipe flame?
4. State how you would ascertain whether the yellow precipitate produced by platinic chloride indicates the presence of a salt of ammonium or potassium, or of both.
5. How can hydric potassic tartrate be distinguished from hydric ammonic tartrate?
6. How can sodium compounds be recognized in the wet way?
7. Which sodic salts are found native?
8. What changes do the following ammonic salts undergo upon ignition:—ammonic chloride, ammonic nitrate, ammonic nitrite, ammonic phosphate, $\mathbf{P}\mathrm{OAmo}_3$, ammonic carbonate, $\mathbf{C}\mathrm{OAmo}_2$, ammonic iodide?
9. How is spongy platinum prepared?
10. How would you test for mere traces of ammonia?
11. How much spongy platinum is obtained from 2·345 grms. of ammonic platinic chloride?

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* For the preparation of Nessler's solution, see Appendix.

12. How much dry ammonia gas by volume (litres) and weight can be obtained by distillation with calcic hydrate from 5 grms. of ammonic chloride?
13. How would you examine a mixture containing ammonic chloride and potassic chloride?
14. 2 grms. of the mixed chlorides of potassium and sodium gave by precipitation with platinic chloride 3.671 grms. of potassic platinic chloride, $2\mathrm{KCl},\mathbf{Pt}\mathrm{Cl}_4$; what is the percentage of potassium and sodium in the mixed chlorides?
15. A mixture of 1·5 grm. of sodic and ammonic chloride lost on ignition ·234 grm.; what is the percentage of ammonic and sodic chloride present in the mixture?
16. Calculate the percentage composition of borax.

4. **MAGNESIUM**, Mg.—Occurs in nature as OXIDE, in the mineral *periclase*, $\mathbf{M}\mathrm{gO}$; as HYDRATE in *brucite*, $\mathbf{M}\mathrm{gHo}_2$; as CARBONATE in *magnesite*, $\mathbf{C}\mathrm{OMgo}''$, and in *hydromagnesite*, $\mathbf{C}_3\mathrm{OHo}_2\mathrm{Mgo}''_4,3\mathbf{O}\mathrm{H}_2$; as DOUBLE CARBONATE in *dolomite*, $\genfrac{}{}{0pt}{}{\mathbf{C}\mathrm{O}}{\mathbf{C}\mathrm{O}}\mathrm{Cao}''\mathrm{Mgo}''$, and *mesitine spar*, $\genfrac{}{}{0pt}{}{\mathbf{C}\mathrm{O}}{\mathbf{C}\mathrm{O}}\mathrm{Mgo}''\mathrm{Feo}''$; as SULPHATE in *epsomite*, $\mathbf{S}\mathrm{OHo}_2\mathrm{Mgo}'',6\mathbf{O}\mathrm{H}_2$; as PHOSPHATE in *wagnerite*, $\mathbf{P}_2\mathrm{O}_2\mathrm{Mgo}''_2,2\left(\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{F}}\mathrm{Mg}''\right)$; as SILICATE in *peridote*, $\mathbf{Si}\mathrm{Mgo}''_2$, *enstatite*, $\mathbf{S}\mathrm{iOMgo}''$, *steatite*, $\mathbf{Si}_4\mathrm{O}_5\mathrm{Mgo}''_3$, *talc*, $\mathbf{S}\mathrm{i}_5\mathrm{O}_6\mathrm{Mgo}''_4$, *serpentine*, $\genfrac{}{}{0pt}{}{\mathbf{Si}\mathrm{HoMgo}''}{\mathbf{Si}\mathrm{HoMgo}''}\mathrm{Mgo}''$, *meerschaum*, $\mathbf{Si}_3\mathrm{O}_2\mathrm{Ho}_4\mathrm{Mgo}''_2$ and in *diopside*, $\genfrac{}{}{0pt}{}{\mathbf{S}\mathrm{iO}}{\mathbf{S}\mathrm{iO}}\mathrm{Cao}''\mathrm{Mgo}''$; and lastly, as BORATE in *boracite*, $\mathbf{B}_8\mathrm{O}_9\mathrm{Mgo}''_3$.

REACTIONS IN THE DRY WAY.

The most characteristic reaction for magnesia in the dry way is the *pale rose* colour which this alkaline earth acquires on moistening with cobaltous nitrate, and then igniting it once more strongly on charcoal.

This colour can, however, only be relied on when no other metallic oxides are present; and as magnesium does not colour the outer blowpipe flame, recourse must almost invariably be had to the reactions in the wet way. Ignition of the sulphate on charcoal in the reducing flame yields the sulphide, $\mathbf{M}\mathrm{gS}$. Prolonged ignition of the carbonate yields caustic magnesia, $\mathbf{M}\mathrm{gO}$, which is almost insoluble in water.

REACTIONS IN THE WET WAY.

For this purpose a SOLUTION OF MAGNESIC CHLORIDE, $\mathbf{M}\mathrm{gCl}_2$, or MAGNESIC SULPHATE, $\mathbf{S}\mathrm{O}_2\mathrm{Mgo}''$, is employed.

Magnesia is not precipitated by ammonia in the presence of ammonic chloride, because it forms a *soluble double chloride*, $2\mathrm{AmCl},\mathbf{M}\mathrm{gCl}_2$. In the absence of ammonic chloride, half the magnesia is precipitated as hydrate, $\mathbf{M}\mathrm{gHo}_2$, thus:—

$$2\mathbf{M}\mathrm{gCl}_2 + 2\mathrm{AmHo} = \mathbf{M}\mathrm{gHo}_2 + \underbrace{2\mathrm{AmCl},\mathbf{M}\mathrm{gCl}_2}_{\text{Soluble double chloride.}}$$

In the presence of ammonic chloride the magnesic hydrate is at once decomposed into magnesic chloride ($\mathbf{M}\mathrm{gHo}_2 + 2\mathrm{AmCl} = \mathbf{M}\mathrm{gCl}_2 + 2\mathrm{AmHo}$), and no precipitation takes place, nor is the double chloride precipitated by ammonic, sodic or potassic carbonate. Hence magnesium cannot be precipitated in Groups III and IV, *provided a sufficient amount of ammonic chloride be present.*

Potassic, sodic, calcic and baric hydrate precipitate *white* **magnesic hydrate**, insoluble in water. Ammonic chloride, as well as other ammonic salts, dissolve it readily, or if originally present, prevent its formation.

Sulphuric, hydrofluosilicic and oxalic acid, $\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}OHo\end{array}\right.$, form soluble magnesic salts.

$\mathbf{P}OHoNao_2$ (**hydric disodic phosphate**), precipitates **hydric magnesic phosphate**, $\mathbf{P}OHoMgo''$.

The precipitation is complete in the presence of ammonic chloride and ammonia. $\mathbf{P}OAmoMgo'',6Aq$, **ammonic magnesic phosphate**, falls as *a white crystalline* precipitate. The separation from a dilute solution of a magnesic salt is promoted by gentle heat, and by stirring with a glass rod. The precipitate is but slightly soluble in water and ammonic salts. In water containing ammonia it is practically insoluble. Dilute mineral acids dissolve it as well as acetic acid. From very dilute solutions the precipitate separates only on standing for about 24 hours in a warm place.

On heating magnesic chloride, $\mathbf{M}gCl_2$, with precipitated mercuric oxide, $\mathbf{H}gO$, **the chloride is converted into oxide,** mercuric chloride, $\mathbf{H}gCl_2$, being volatilized. This experiment must be conducted in a cupboard which is provided with a good indraught of air, and is in connection with a chimney flue.

Methods for the recognition of Mg, K, Na, and Am will readily suggest themselves, if we bear in mind—

1st. *The volatility of ammonic salts* (phosphates and borates excepted).
2nd. *The insolubility of* $\mathbf{M}gHo_2$ *in water.*
3rd. *The insolubility of* $2KCl,\mathbf{P}tCl_4$ *in alcohol.*
4th. The *intense yellow coloration* which sodium imparts to the blowpipe flame.

A solution containing salts of Mg, K, Na, and Am, may be examined as follows:—

1st. Heat a portion with NaHo; ammonia gas is given off, which is recognized by its pungent odour, etc.—**presence of Am.**

2nd. To a second portion add AmCl, AmHo, and $\mathbf{P}OHoNao_2$, a *white crystalline* precipitate indicates the **presence of Mg.**

3rd. Evaporate a third portion to dryness and ignite strongly. Extract with hot water, and add $\mathbf{B}aHo_2$, till the whole of the Mg is precipitated as $\mathbf{M}gHo_2$; filter. To the filtrate add $\mathbf{C}OAmo_2$, as long as a precipitate is produced, and filter again. Evaporate the filtrate to dryness, and ignite strongly to expel ammonic salts. Dissolve the residue in a little water, filter off a trace of $\mathbf{M}gO$ (if any), and test filtrate for K by means of $\mathbf{P}tCl_4$; a *yellow crystalline* precipitate—**presence of K,** and for Na by heating on a platinum wire before the blowpipe flame; a *golden yellow flame* indicates the **presence of Na.**

QUESTIONS AND EXERCISES.

1. How is magnesic sulphate prepared—1st, from *magnesite*; 2nd, from *dolomite*?
2. Which are the most important magnesium minerals? Give constitutional and graphic formulæ.
3. How is magnesium detected in the dry way?
4. Explain the action which ammonia, potassic hydrate, and sodic carbonate have upon solutions of magnesic salts in the presence of ammonic salts, and also without them.
5. How is magnesic hydrate obtained from soluble magnesic salts?
6. Describe fully the most characteristic reaction for magnesic salts in the wet way.
7. How is magnesic chloride converted into oxide in the dry way?
8. How is magnesium separated from potassium and sodium?
9. Calculate the percentage composition of *magnesite* and *epsomite*.
10. How much crystallised magnesic sulphate, $\mathbf{S}OHo_2Mgo'',6\mathbf{O}H_2$, can be prepared from one ton of pure *magnesite*?

CHAPTER III.

REACTIONS OF THE METALS OF GROUP IV.

THIS group comprises the metals BARIUM, STRONTIUM, CALCIUM, which are precipitated by ammonic carbonate from an ammoniacal solution in the presence of ammonic chloride. The latter prevents the precipitation of magnesium (if present in sufficient quantities).

1. BARIUM, Ba.

—Occurs in nature chiefly in the form of *heavy spar*, $\mathbf{S}O_2Bao''$, and as *witherite*, $\mathbf{C}OBao''$.

REACTIONS IN THE DRY WAY.

Barium compounds, when heated on platinum wire in the inner blowpipe flame, impart a **yellowish green** colour to the outer flame.

Heavy spar heated on charcoal in the reducing flame is reduced to baric sulphide, $\mathbf{Ba}S$, which fuses readily. This reaction is made use of to prepare, on a manufacturing scale, soluble baric salts from the sulphate. Baric carbonate is decomposed only by ignition to a strong white heat.

REACTIONS IN THE WET WAY.

Baric salts are obtained by dissolving the native carbonate or *witherite* in acids.* *Heavy spar* is attacked by alkaline carbonates at a high temperature. By mixing on a small scale finely powdered baric sulphate with three to four times its weight of fusion mixture and heating in a platinum crucible over a gas flame, it is converted into baric carbonate, thus:—

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* Dilute acids (HCl or $\mathbf{N}O_2Ho$) should be employed, as the baric chloride and baric nitrate, which result from the action of these acids upon witherite, are insoluble in the concentrated acids.

$$2\mathbf{S}O_2Bao'' + \mathbf{C}ONao_2,\mathbf{C}OKo_2 = \underset{\text{Insol. in water.}}{2\mathbf{C}OBao''} + \underset{\text{Soluble in water.}}{\mathbf{S}ONao_2,\mathbf{S}O_2Ko_2}.$$

On extracting the fused mass with hot water and filtering, $\mathbf{C}OBao''$ is left, from which, by the addition of the respective acids, small quantities of the different baric salts can be prepared.

The same applies to *celestine*, $\mathbf{S}O_2Sro''$.

A SOLUTION OF BARIC CHLORIDE, $\mathbf{B}aCl_2$, is employed.

$\mathbf{C}OAmo_2$ (**group-reagent**) precipitates *white* **baric carbonate**, $\mathbf{C}OBao''$, soluble with decomposition in acids; somewhat soluble in ammonic chloride. With carbonic acid it forms a soluble acid carbonate or dihydric dicarbonate, $\mathbf{C}_2O_2Ho_2Bao''$, but is reprecipitated on boiling with evolution of carbonic anhydride.

$\mathbf{C}ONao_2$ and $\mathbf{C}OKo_2$, same precipitate.

KHo and NaHo give from concentrated solutions a *voluminous* precipitate of **baric hydrate**, $\mathbf{B}aHo_2$, soluble in water. A solution of the hydrate in water is known as *baryta-water*. It possesses a strong alkaline reaction, and great affinity for carbonic anhydride.

AmHo gives no precipitate.

$\mathbf{S}O_2Ho_2$, as well as all **soluble sulphates**, precipitate *heavy white granular* **baric sulphate**, $\mathbf{S}O_2Bao''$, even from very dilute solutions of baric salts, insoluble in water, dilute acids and alkalies; soluble in concentrated boiling sulphuric acid, with formation of dihydric baric disulphate, $\mathbf{S}_2O_4Ho_2Bao''$. The presence of an alkaline citrate greatly interferes with its precipitation. Solutions of strontic or calcic sulphate (two sulphates which are but slightly soluble in water, especially the former), constitute the most delicate test for barium. Baric sulphate is insoluble in ammonic sulphate, $\mathbf{S}O_2Amo_2$. —(DISTINCTION OF BARIUM FROM STRONTIUM AND CALCIUM).

$\mathbf{P}OHoNao_2$ (**hydric disodic phosphate**) gives from neutral or alkaline solutions a *white* precipitate of **hydric baric phosphate**, $\mathbf{P}OHoBao''$, readily soluble in dilute nitric, hydrochloric or *acetic* acid. Perceptibly soluble in ammonic chloride.

$\left\{\begin{matrix}\mathbf{C}OAmo\\ \mathbf{C}OAmo\end{matrix}\right.$ (**Ammonic oxalate**) gives from a moderately dilute solution of a baric salt a *white pulverulent* precipitate of **baric oxalate**, $\left\{\begin{matrix}\mathbf{C}O\\ \mathbf{C}O\end{matrix}\right.Bao''$, soluble in dilute nitric or hydrochloric acid. Soluble also in oxalic and acetic acids when freshly precipitated.

$\mathbf{Cr}O_2Ko_2$ (**Potassic chromate**) gives a *yellow* precipitate of **baric chromate**, $\mathbf{Cr}O_2Bao''$, readily soluble in nitric, hydrochloric or chromic acid ($\mathbf{Cr}O_2Ho_2$)—reprecipitated by ammonia (DISTINCTION FROM STRONTIUM AND CALCIUM WHICH ARE NOT PRECIPITATED FROM DILUTE SOLUTIONS).

$2HF,\mathbf{Si}F_4$ (**Hydrofluosilicic acid**) gives a *white crystalline* precipitate of **baric silicofluoride**, $\mathbf{B}aF_2,\mathbf{Si}F_4$, which subsides quickly, especially upon the addition of an equal bulk of alcohol. It is somewhat soluble in water, insoluble in alcohol and dilute acids. (DISTINCTION OF BARIC FROM STRONTIC AND CALCIC SALTS, WHICH GIVE NO PRECIPITATE.)

Barium, in baric peroxide, is combined with two atoms of oxygen, which are linked to the metal by one of their bonds only, the other bonds being linked together. *Baric peroxide* is a powerful oxidising agent. It is formed by passing oxygen over baric oxide, heated to dull redness, thus:—$2\mathbf{Ba}O + O_2 = 2\mathbf{Ba}O_2$. Heat splits it up again into baric oxide and oxygen; and dilute acids liberate a molecule of hydroxyl, Ho_2, thus:—$\mathbf{Ba}O_2 + 2HCl = \mathbf{Ba}Cl_2 + Ho_2$.

Soluble baric salts, such as baric chloride, nitrate or acetate, constitute exceedingly useful reagents for the detection of acids, on account of the metal barium forming insoluble salts with most acids.

QUESTIONS AND EXERCISES.

1. How can baric sulphate be converted into baric nitrate or chloride?
2. Which are the natural compounds of barium?
3. Express in symbolic equations the different reactions for barium.
4. Which are the most delicate reactions for barium?
5. How can barium be separated from strontium and calcium?
6. 1·235 grm. of *witherite* gave ·965 grm. of baric sulphate; what is the percentage of barium and of baric carbonate in the mineral?
7. How is $\mathbf{Ba}\left.\begin{matrix}O\\O\end{matrix}\right\}$ prepared, and what reaction takes place when it is suspended in water and treated with carbonic anhydride?
8. A sample of *heavy spar* contains 96·5 per cent. of pure sulphate. How much baric sulphide, and how much baric nitrate can be obtained from 1 cwt. of the mineral?

2. **STRONTIUM**, Sr''.—Occurs in nature as SULPHATE, in the mineral *celestine*, $\mathbf{S}O_2Sro''$; and as CARBONATE or *strontianite*, $\mathbf{C}OSro''$.

EXAMINATION IN THE DRY WAY.

Strontium compounds, when heated on platinum wire in the inner flame, colour the outer flame **crimson.**

Celestine, heated on charcoal in the reducing flame, is converted into sulphide, $\mathbf{Sr}S$, from which the chloride may be prepared for blowpipe and other reactions, by treating the residue with hydrochloric acid.

REACTIONS IN THE WET WAY.

We use A SOLUTION OF STRONTIC CHLORIDE, $\mathbf{Sr}Cl_2$.

$\mathbf{C}OAmo_2$ **(group-reagent)** gives a *white* precipitate of **strontic carbonate**, $\mathbf{C}OSro''$, less soluble in ammonic chloride than the corresponding baric carbonate; soluble in dilute acids. Carbonic acid produces the soluble dihydric strontic dicarbonate, $\mathbf{C}_2O_3Ho_2Sro''$, which is decomposed on boiling into normal carbonate, carbonic anhydride and water.

$\mathbf{C}ONao_2$ and $\mathbf{C}OKo_2$, same precipitate.

$\mathbf{S}O_2Ho_2$, or **soluble sulphates**, produces a *white* precipitate of **strontic sulphate**, $\mathbf{S}O_2Sro''$. From *dilute* solutions a precipitate appears *only after some time.* Heat assists the precipitation. The precipitate dissolves perceptibly in hydrochloric or nitric acid, but is *insoluble in alcohol*. It is insoluble also in a concentrated solution of ammonic sulphate, $\mathbf{S}O_2Amo_2$ (DISTINCTION BETWEEN STRONTIUM AND CALCIUM).

A solution of strontic sulphate in water precipitates baric salts.

$\left\{\begin{matrix}\mathbf{C}OAmo\\ \mathbf{C}OAmo\end{matrix}\right.$ **(Ammonic oxalate)** precipitates strontic salts more readily than baric salts. The *white* precipitate of **strontic oxalate,** $\left\{\begin{matrix}\mathbf{C}O\\ \mathbf{C}O\end{matrix}\right.Sro''$, is readily soluble in dilute nitric or hydrochloric acid; somewhat soluble in ammonic chloride; but sparingly soluble in oxalic or acetic acid.

QUESTIONS AND EXERCISES.

1. Which are the principal strontium minerals?
2. How are strontic chloride and nitrate prepared—1st. from *strontianite*; 2nd. from *celestine*?
3. Which are the most characteristic reactions for strontium?
4. How can strontium be distinguished from barium?
5. What is the percentage of strontium in *strontianite* and in *celestine*?
6. How can strontium be separated from calcium?

3. **CALCIUM,** Ca''.—Occurs in nature in the mineral, vegetable and animal kingdom in vast masses, in combination with carbonic, sulphuric, silicic and phosphoric acids. In plants it occurs combined with carbonic, sulphuric and phosphoric acids; in animals, combined with phosphoric and carbonic acids. It is occasionally also found in minerals which result from the action of acids (such as nitric or arsenic acid) upon *calc spar*.

The principal calcium minerals are the various CALCIC CARBONATES, differing in physical properties or in crystalline structure, such as *calc spar*, $\mathbf{C}OCao''$ (containing occasionally barium, magnesium, iron, manganese, lead, in variable proportions, and passing gradually into *baryto-calcite* and *dolomite*, *siderite*, *diallogite* and *plumbocalcite*), *arragonite*, *marble*, *limestone*, *chalk*; the SULPHATES, such as *gypsum*, $\mathbf{S}Ho_4Cao''$, *anhydrite*, $\mathbf{S}O_2Cao''$, *alabaster*, *selenite*; the PHOSPHATES, such as *apatite*, $\mathbf{P}_3O_3Cao''_4\left(\begin{matrix}O\\F\end{matrix}Ca''\right)$, *bone-earth*, $\mathbf{P}_2O_2Cao''_3$; and *fluor spar*, $\mathbf{Ca}F_2$.

REACTIONS IN THE DRY WAY.

Most calcium compounds, when heated in the inner flame of the blowpipe, colour the outer flame **yellowish red**; calcic phosphate and borate excepted. The presence of barium or strontium entirely obscures the calcium reaction.

Calcic carbonate when strongly ignited becomes converted into caustic or quicklime, $\mathbf{Ca}O$, which reacts alkaline. It combines with water very eagerly, evolving much heat, and is converted into calcic hydrate, $\mathbf{Ca}Ho_2$ (slaked lime). Calcic sulphate is converted into calcic sulphide, $\mathbf{Ca}S$, when ignited on charcoal in the reducing flame. The mass reacts likewise alkaline.

REACTIONS IN THE WET WAY.

Calcic salts are readily prepared from pure *calc spar* or *marble*, by means of dilute acids.

We employ A SOLUTION OF CALCIC CHLORIDE, $\mathbf{Ca}\mathrm{Cl}_2$.

$\mathbf{C}\mathrm{OAmo}_2$ (**group-reagent**) precipitates *white* **calcic carbonate**, $\mathbf{C}\mathrm{OCao}''$, which is bulky and amorphous at first, but on heating becomes rapidly crystalline. The precipitate is somewhat soluble in ammonic chloride, when freshly precipitated.

$\mathbf{C}\mathrm{ONao}_2$ and $\mathbf{C}\mathrm{OKo}_2$, same reaction.

$\mathbf{S}\mathrm{O}_2\mathrm{Ho}_2$, or **soluble sulphates**, precipitates from concentrated solutions of a calcic salt *white* **calcic sulphate**, $\mathbf{S}\mathrm{OHo}_2\mathrm{Cao}'' + \mathrm{Aq}$, soluble in much water, and still more soluble in acids. A precipitate is obtained on the addition of alcohol from solutions which are too dilute to be precipitated by sulphuric acid or a soluble sulphate. Calcic sulphate dissolves readily on boiling in a concentrated solution of ammonic sulphate.

A solution of calcic sulphate precipitates baric and strontic salts.

$\mathbf{P}\mathrm{OHoNao}_2$ (**hydric disodic phosphate**) gives a *bulky white* precipitate of **tricalcic phosphate**, $\mathbf{P}_2\mathrm{O}_2\mathrm{Cao}''_3$, soluble in dilute hydrochloric or nitric acid, and soluble in acetic acid; reprecipitated by ammonia.

$\left\{\begin{array}{l}\mathbf{C}\mathrm{OAmo}\\ \mathbf{C}\mathrm{OAmo}\end{array}\right.$ (**ammonic oxalate**) produces from a very dilute solution of a calcic salt a *white pulverulent* precipitate of **calcic oxalate**, $\left\{\begin{array}{l}\mathbf{C}\mathrm{O}\\ \mathbf{C}\mathrm{O}\end{array}\right.\mathrm{Cao}'' + 2\mathrm{Aq}.$, readily soluble in hydrochloric or nitric acid; not perceptibly soluble in oxalic or acetic acid. On gentle ignition calcic oxalate breaks up into calcic carbonate, and carbonic oxide gas ($\mathbf{C}\mathrm{O}$), and on igniting very strongly it leaves caustic lime.

Soluble calcic salts, such as the chloride or nitrate, constitute very important reagents for the detection of acids, on account of the metal calcium forming insoluble salts with most acids.

QUESTIONS AND EXERCISES.

1. Which are the most important natural lime compounds?
2. Give graphic formulæ for *gypsum*, *anhydrite*, *calc spar*, *fluor spar*, *apatite*.
3. Which are the most delicate reactions for calcium in the wet way?
4. How is *arragonite* converted into calcic oxalate?
5. Calculate the percentage composition of *bone-ash*.
6. Explain the terms—*caustic* or *quicklime*, *slaked lime*, *lime water*.
7. How is a solution of calcic sulphate employed for the detection of barium and strontium?

Separation of Barium, Strontium, and Calcium.—Barium minerals frequently contain strontium and calcium, and strontium minerals barium and calcium as well. The separation of these metals is based upon—

1st. The *insolubility* of $\mathbf{Ba}\mathrm{Cl}_2$ in *absolute alcohol* ($\mathbf{Sr}\mathrm{Cl}_2$ and $\mathbf{Ca}\mathrm{Cl}_2$ being soluble).

2nd. The *insolubility* of $\mathbf{N}_2\mathrm{O}_4\mathrm{Bao}''$, and $\mathbf{N}_2\mathrm{O}_4\mathrm{Sro}''$ in *absolute alcohol* (calcic nitrate being soluble).

A hydrochloric acid solution of the mineral containing Ba and Sr, or Sr and Ca, or possibly Ba, Sr and Ca, is prepared, and the solution evaporated to dryness and gently ignited.

Barium is separated from strontium and calcium, by digesting the finely divided residue with absolute alcohol, and separating the undissolved $\mathbf{Ba}Cl_2$ by filtration.

Strontium is separated from calcium by evaporating or distilling off the absolute alcohol, which contains the $\mathbf{Sr}Cl_2$ and $\mathbf{Ca}Cl_2$; precipitating with $\mathbf{C}OAmo_2$, and conversion of the strontic and calcic carbonates into nitrates by means of dilute nitric acid. The solution of the two nitrates is evaporated to dryness, and absolute alcohol added, when calcic nitrate is dissolved out, strontic nitrate being insoluble in absolute alcohol.

On setting fire to alcohol containing baric, strontic, or calcic chloride (or nitrate) in solution, the alcohol is seen to burn with the characteristic colour observed when traces of these salts were heated on a platinum wire.

Several methods of recognizing and of separating the metals of Group IV will suggest themselves.

It is often useful to ascertain whether one or two, or all the metals of this group are present in a solution. This can be done by adding to their *neutral* solution a solution of $\mathbf{Cr}O_2Ko_2$, or $2HF,\mathbf{Si}F_4$. A yellow or a white crystalline precipitate indicates barium. To the filtrate add $\mathbf{S}O_2Cao''$; a precipitate forms perhaps only after some time, proving the presence of strontium; or the solution remains clear, in which case calcium only need be looked for, the presence of which is indicated by the precipitate which $\left\{\begin{matrix}\mathbf{C}OAmo\\ \mathbf{C}OAmo\end{matrix}\right.$ produces from another portion of the largely diluted solution.

The student will have no difficulty in drawing up a tabular analytical scheme[*] based upon :—

1st. The *insolubility of* $\mathbf{Ba}Cl_2$ and $\mathbf{N}_2O_4Sro''$ *in absolute alcohol.*

2nd. The *insolubility of* $\mathbf{Ba}Cl_2$ *in absolute alcohol* and *that of* $\mathbf{S}O_2Sro''$ *in a concentrated solution of* $\mathbf{S}O_2Amo_2$.

3rd. The *insolubility of* $\mathbf{Ba}F_2$, $\mathbf{Si}F_4$, or $\mathbf{Cr}O_2Bao''$, *as well as of* $\mathbf{S}O_2Sro''$ *in water; calcic sulphate being sufficiently soluble to give a precipitate with ammonic oxalate.*

PRACTICAL EXERCISES[†] ON GROUPS IV AND V.

You are requested to analyze—

1. A solution of salts of the metals K, Mg, and Ba.
2. A mixture (about ·500 grm.) of the solid salts NaCl, $\mathbf{Sr}Cl_2$, and *magnesia alba* ($\mathbf{C}_2Ho_4Mgo''_4$).
3. A mixture of the solid salts AmCl, $\mathbf{Ba}Cl_2$ and $\mathbf{C}OCao''$.
4. A mixture of the salts AmCl and $\mathbf{S}O_2Mgo''$.
5. A mixture containing finely powdered marble, baric carbonate and common salt.
6. A solution of $\mathbf{Ba}Cl_2$ and $\mathbf{Sr}Cl_2$, containing ·010 grm. of Ba and ·100 grm. of Sr.
7. A solution of NaCl, KCl, and $\mathbf{Mg}Cl_2$, containing ·020 grm. of K, ·200 grm. of Na, and ·050 grm. of Mg.
8. A solution of $\mathbf{Sr}Cl_2$ and $\mathbf{Ca}Cl_2$, containing ·050 grm. of Sr, and ·500 grm. of Ca.

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[*] Table IV in the analytical tables at the end of the book contains a scheme embodying method 2.

[†] As a control upon the work done in a laboratory the analytical results should be carefully recorded (as far as possible, in a tabular form), and should be open to inspection.

CHAPTER IV.

REACTIONS OF THE METALS OF GROUP III, OR $\mathbf{S}Am_2$ GROUP.

GROUP III comprises the metals NICKEL, COBALT, MANGANESE, ZINC, IRON, CHROMIUM, ALUMINIUM, likewise the phosphates of these metals, and of MAGNESIUM, BARIUM, STRONTIUM, and CALCIUM.

1. Add to a solution[*] containing $\mathbf{M}_2O_4Coo''$, $\mathbf{Fe}_2Cl_6$, and calcic phosphate, dissolved in a little dilute hydrochloric acid, a concentrated solution of ammonic chloride, and then ammonia. A precipitate is produced. Filter and add to the filtrate $\mathbf{S}Am_2$. A further precipitation takes place; the precipitate is black.

This shows *that some members of this group are precipitated by AmCl and AmHo; others only on the addition of* $\mathbf{S}Am_2$.

2. Add to a solution of $\mathbf{Fe}_2Cl_6$, $\mathbf{Cr}_2Cl_6$, and $\mathbf{Al}_2Cl_6$, ammonic chloride and ammonia, till it is distinctly ammoniacal. A bulky gelatinous precipitate is obtained. Filter. Add to the clear filtrate $\mathbf{S}Am_2$; no further precipitation takes place.

Showing *that Iron, Chromium, and Aluminium are precipitated (as hydrates) from their saline solutions by AmCl and AmHo alone, without the aid of* $\mathbf{S}Am_2$. (Ammonic chloride has no share in the precipitation, but prevents the solubility of the aluminic hydrate in excess of the precipitant, as well as the precipitation of magnesium, as hydrate).

3. Dissolve some baric, strontic, calcic, and magnesic phosphates in dilute hydrochloric acid, and cautiously add to the solution ammonia. No precipitate is produced till the free acid has been neutralized (with formation of ammonic chloride), when the phosphates are reprecipitated. Filter and add $\mathbf{S}Am_2$ to the filtrate. No further precipitation takes place.

This shows *that the phosphates of the alkaline earthy metals are precipitated by ammonia alone.*

4. Dissolve some phosphates of Ni, Co, Mn, Zn, and Fe in dilute hydrochloric acid.[†] To one portion of the solution add AmCl and AmHo. A precipitate is formed. The phosphates are reprecipitated. Filter and add $\mathbf{S}Am_2$; a further precipitate is produced.

Showing *that the phosphates of these metals are not entirely precipitated by ammonic chloride and ammonia.*

Thus far we have seen that these two reagents precipitate:—

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[*] Solutions containing ·005 grm. of the metal in every c.c. are readily prepared, and should be kept for use. 5 c.c. of each solution will be found a convenient quantity.

[†] This solution may also be prepared by adding hydric disodic phosphate to solutions of the above metals as long as a precipitate forms, and dissolving the precipitate in a little hydrochloric acid.

Nickelous phosphate
Cobaltous „
Manganous „
Zincic „
Ferric „
Ferric hydrate
Chromic „
Aluminic „

Chromic phosphate
Aluminic „
Baric „
Strontic „
Calcic „
Magnesic „

5. To a solution of $\mathbf{S}O_2Nio''$, $\mathbf{N}_2O_4Coo''$, $\mathbf{S}O_2Zno''$, and $\mathbf{Mn}Cl_2$ (free from Fe), add AmCl in considerable excess, and then AmHo in slight excess. No precipitate is obtained, the precipitate first produced by AmHo being soluble in the ammonic salt. To one portion of the solution add strong sulphuretted hydrogen water (or pass a current of sulphuretted hydrogen gas); a copious precipitate is produced, consisting of $\mathbf{Ni}S$ and $\mathbf{Co}S$ (black), $\mathbf{Zn}S$ (white), and $\mathbf{Mn}S$ (buff coloured).

This shows *that Nickel, Cobalt, Manganese, and Zinc salts are not precipitated by AmCl and AmHo, but by* $\mathbf{S}Am_2$.

On exposing the other portion of the solution for some time to the air, it is seen to turn turbid, where it is in contact with the air. Heat and shake the solution and the turbidity increases rapidly.

Showing *that AmCl and AmHo produce, under favourable conditions, a partial precipitation.*

6. To another portion of the solution of the phosphates of Ni, Co, Mn, Zn, and Fe (see 4), add AmCl, AmHo, and $\mathbf{S}Am_2$, without first separating by filtration the precipitate produced by AmCl and AmHo. THE PHOSPHATES OF Co, Ni, Mn, Zn, AND Fe, which may be present in the hydrochloric acid solution, ARE DECOMPOSED INTO SULPHIDES, AND AMMONIC PHOSPHATE IS LEFT IN SOLUTION.

7. To a solution of $\mathbf{Fe}_2Cl_6$, add AmCl and AmHo, a reddish-brown precipitate of ferric hydrate, $\mathbf{Fe}_2Ho_6$ is produced, which on the addition of $\mathbf{S}Am_2$ turns instantaneously black.

This shows *that iron is first precipitated as hydrate, and is subsequently converted into sulphide.* Chromic and aluminic chlorides are precipitated under the same circumstances as hydrates; but they form no sulphides in the wet way.

We may then sum up by saying that the group reagents, AmCl and AmHo, for reasons stated under 4 and 5, cannot thoroughly separate some of the members of Group III from others, and that $\mathbf{S}Am_2$ should invariably be added as well. The three reagents* precipitate:—

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* Add AmHo to a solution of baric, strontic, calcic and magnesic oxalates in dilute hydrochloric acid, as long as a white precipitate is obtained. The oxalates of the alkaline earths are reprecipitated, as soon as the hydrochloric acid which (as in the case of the corresponding phosphates) holds them in solution is completely neutralized.

The same applies to the fluorides, borates, tartrates, citrates, etc., of these earthy bases, which are precipitated by AmHo, although in the presence of much AmCl they are, to a great extent, held in solution.

Silicic acid and silicates, soluble in hydrochloric acid, are likewise precipitated by AmCl and AmHo as gelatinous silica, $\mathbf{Si}Ho_4$.

In order to avoid complicating the qualitative course, it is usually preferred to evaporate the hydrochloric acid filtrate from Group II to complete dryness, with the addition towards the end of the evaporation of a little concentrated

1. SULPHIDES—

$\mathbf{Ni}S$	black
$\mathbf{Co}S$	black
$\mathbf{Mn}S$	buff
$\mathbf{Zn}S$	white
$\mathbf{Fe}S$	black.

2. HYDRATES—

$\mathbf{Cr}_2Ho_6$	green
$\mathbf{Al}_2Ho_6$	white.

3. PHOSPHATES of Cr, Al, Ba, Sr, Ca, and Mg.

NICKEL, Ni'' AND ^{iv}.—Occurs in nature as SULPHIDE, $\mathbf{Ni}S''$, in *capillary pyrites*, *hair nickel*, or *millerite;* as ARSENIDE, in *arsenical nickel*, $\left\{\begin{matrix}{}''\mathbf{As}' \\ {}''\mathbf{As}'\end{matrix}\right.Ni''$, and in *copper nickel*, $\left\{\begin{matrix}{}'\mathbf{As}''Ni'' \\ {}'\mathbf{As}''Ni''\end{matrix}\right.$; as ANTIMONIDE, in $\left\{\begin{matrix}{}'\mathbf{Sb}''Ni'' \\ {}'\mathbf{Sb}''Ni''\end{matrix}\right.$, *antimony nickel*, combined with SULPHIDE, as in *nickel glance* or *grey nickel ore*, $\left\{\begin{matrix}{}''\mathbf{As}' \\ {}''\mathbf{As}'\end{matrix}\right.Ni,\mathbf{Ni}^{iv}S_2$, as *antimony nickel glance*, $\left\{\begin{matrix}{}''\mathbf{Sb}' \\ {}''\mathbf{Sb}'\end{matrix}\right.Ni,\mathbf{Ni}^{iv}S_2$; also in the form of minerals which are the result of the oxidation of other nickel minerals, *e.g.*, as *nickel ochre*, $\mathbf{As}_2O_2Nio''_3$, and *emerald nickel*, $\mathbf{C}(ONi''Ho)_2Nio''$, $5\mathbf{O}H_2$.

REACTIONS IN THE DRY WAY.

When nickelous salts are heated on charcoal with dry $\mathbf{C}ONao_2$, in the *inner* blowpipe flame, they are reduced to a grey metallic powder which is magnetic. Heated on a *borax* bead, in the *outer* flame, nickel compounds yield an intensely coloured glass, which appears **hyacinth red to violet brown** when hot, and **yellowish to sherry red** when cold (according to the quantity of nickel present). On fusing a little nitre in the bead, the colour is changed to blue or dark purple, whereby nickel compounds may be distinguished from iron. Heated in the *reducing* flame the colour disappears, and the bead assumes a turbid grey appearance, owing to finely divided particles of metallic nickel. The reactions with microcosmic salt are similar; but the bead becomes almost colourless when cold.

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nitric acid, whenever AmCl and AmHo produce a precipitate. By these means silicic anhydride, $\mathbf{Si}O_2$, is left behind insoluble in acids; the fluorides and borates are for the most part decomposed, hydrofluoric and boric acid being volatilized. Oxalates are destroyed with evolution of carbonic anhydride by the oxidizing action of the nitric acid, and tartrates, etc., are broken up by gentle ignition into carbon and volatile gaseous products; ferrous salts are converted into ferric salts, and on extracting the ignited residue with a little concentrated hydrochloric acid, the metals are obtained in solution as chlorides, together only with the phosphates of the alkaline earths, earthy and metallic bases.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF NICKELOUS SULPHATE, $\mathbf{S}O_2Nio''$.

$\mathbf{S}Am_2$ (**group-reagent**) gives a *black* precipitate of **nickelous sulphide**, $\mathbf{Ni}S$, slightly soluble in excess of the reagent, especially in the presence of free ammonia, forming a dark brown solution, whence $\mathbf{Ni}S$ is reprecipitated on boiling. The presence of ammonic chloride, (or better still, $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OAmo\end{matrix}\right.$, ammonic acetate) assists the precipitation. $\mathbf{Ni}S$ dissolves with difficulty in dilute hydrochloric acid, readily in nitric acid or aqua regia, and is but slightly soluble in acetic acid.

$\mathbf{S}H_2$ gives no precipitate in an acid solution, and a partial precipitate only from a salt of nickel with a mineral acid; but produces readily a precipitate from a solution of nickelous acetate, or a nickelous salt mixed with an alkaline acetate.

NaHo or KHo precipitates *an apple green* **hydrate**, $\mathbf{Ni}Ho_2$, insoluble in excess, soluble in ammonic salts to a greenish blue fluid. $\mathbf{Ni}Ho_2$ leaves on ignition $\mathbf{Ni}O$. It does not absorb oxygen from the air.

AmHo produces a slight *greenish* precipitate, readily soluble to a blue fluid. No precipitate in presence of ammonic chloride.

$\mathbf{C}ONao_2$ precipitates an *apple green* **basic carbonate**, varying in composition.

$\mathbf{C}OAmo_2$, same precipitate, readily soluble in excess to a greenish blue solution.

KCy (free from cyanate (CyKo) and carbonate[*]) gives a *yellowish green* precipitate of **nickelous cyanide**, $\mathbf{Ni}Cy_2$, which dissolves readily in excess of potassic cyanide to a brownish yellow solution, containing a double cyanide of nickel and potassium, $2KCy, \mathbf{Ni}Cy_2$. On adding a dilute acid (HCl or $\mathbf{S}O_2Ho_2$), $\mathbf{Ni}Cy_2$ is reprecipitated, and KCy is decomposed with evolution of HCy. Boiling with hydrochloric acid decomposes the $\mathbf{Ni}Cy_2$ likewise.

The solution of the double cyanide is not altered by boiling with excess of HCy, but is decomposed by chlorine, or on the addition of a concentrated solution of sodic hypochlorite, ClNao, *black* **nickelic hydrate**, $'\mathbf{Ni}'''_2Ho_6$, being precipitated, thus :—

$$2\mathbf{Ni}Cy_2 + ClNao + 5\mathbf{O}H_2 = \mathbf{Ni}_2Ho_6 + NaCl + 4HCy.$$

Nickelic hydrate may also be obtained by passing chlorine through water, in which nickelous hydrate is suspended. HCl decomposes the tetrad nickel-compound into $\mathbf{Ni}Cl_2$ and free chlorine.

QUESTIONS AND EXERCISES.

1. Express in symbolic equations the reactions for nickel in the wet way.

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[*] It is preferable to add hydrocyanic (prussic) acid, HCy, to a neutral solution of a nickelous salt, and then KHo drop by drop, till the yellowish green precipitate is redissolved. Great caution has to be observed on account of the highly poisonous nature of HCy.

2. State which are the principal nickel minerals, and translate into graphic formulæ the constitutional formulæ of *emerald nickel, antimony nickel*, nickelous nitrate and acetate.
3. How many oxides of nickel are there; and how would you prepare them from a solution of nickelous sulphate?
4. How would you recognize the presence of Ni and As in *arsenical nickel?*
5. 50 cubic centimetres of a solution of nickelous sulphate yield on precipitation with KHo and ignition ·370 grm. of $\mathbf{N}iO$, how much Ni is contained in 1 c.c. of the solution, and how much nickelous sulphate ($\mathbf{S}OHo_2Nio'',6\mathbf{O}H_2$) must be dissolved in a litre of water to obtain a solution of the above strength?
6. Calculate the percentage composition of *capillary pyrites*.

COBALT, Co'' and ^{iv}.—Occurs in nature as SULPHIDE or *cobalt pyrites*, $\mathbf{Co}_2S_3$ or $\left\{\begin{matrix}\mathbf{Co}S''\\ \mathbf{Co}S''\end{matrix}\right.S''$; as ARSENIDE in $\left\{\begin{matrix}''\mathbf{As}'\\ ''\mathbf{As}'\end{matrix}\right.\mathbf{Co}''$, tin-white cobalt or *smaltine* (*speiss cobalt*), as SULPHARSENIDE, or *cobalt glance*, $\left\{\begin{matrix}''\mathbf{As}'\\ ''\mathbf{As}'\end{matrix}\right.Co,\mathbf{Co}^{iv}S_2$; also in the form of products of oxidation, such as *cobalt vitriol*, $\mathbf{S}OHo_2Coo'',6\mathbf{O}H_2$, as *arseniate*, $\mathbf{As}_2O_2Coo''_3,8\mathbf{O}H_2$, in *cobalt bloom*, and generally in small quantity in *nickel* and *iron ores*.

REACTIONS IN THE DRY WAY.

Cobalt is usually detected with comparative facility. Cobalt minerals containing sulphur or arsenic are roasted on charcoal, or in a glass tube, when $\mathbf{S}O_2$ and $\mathbf{As}_2O_3$ are evolved. The residue is then introduced into a *borax* bead, and heated in the *outer* flame, when a *fine* **blue**, so-called cobalt glass, is obtained. This colour remains the same both in the outer and inner, or *reducing* flame. In cases where much Mn, Fe, Cu, or Ni are mixed with Co, the blue appears distinctly only after the bead has been heated for some time in the reducing flame. Microcosmic salt gives the same blue bead. Heated on charcoal, with $\mathbf{C}ONao_2$ in the reducing flame, cobalt separates as a grey metallic powder which is attracted by the magnet.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF COBALTOUS NITRATE, $\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Coo''$.

$\mathbf{S}Am_2$ **(group-reagent)** gives a *black* precipitate of **cobaltous sulphide**, $\mathbf{Co}S$, insoluble in excess of the reagent; scarcely soluble in acetic acid, and very difficultly soluble in dilute hydrochloric or sulphuric acid; but readily soluble in aqua regia upon the application of heat. Hence a black residue left on treating the $\mathbf{S}Am_2$ precipitate of Group III with dilute hydrochloric acid, indicates probably the presence of $\mathbf{Co}S$ or $\mathbf{N}iS$.

$\mathbf{S}H_2$ gives no precipitate from an acid solution, but precipitates Co partially from a neutral solution, and wholly from a solution of cobaltous acetate, or from a solution of a cobaltous salt containing a mineral acid, and completely on the addition of an alkaline acetate, and upon heating.

KHo or NaHo gives a precipitate of a *blue* **basic salt**, which turns *olive green* on exposure to air, owing to the absorption of oxygen. On heating, a *rose red* **cobaltous hydrate,** $\mathbf{Co}Ho_2$, is obtained, which, however, contains mostly a small amount of dark brown cobaltic oxide, $'\mathbf{Co}'''_2O_3$. Ammonic carbonate dissolves the precipitate (after filtration and washing) to an intensely violet-red fluid.

By suspending $\mathbf{Co}Ho_2$ in water, and passing a current of chlorine into it, a black powder, $\mathbf{Co}_2Ho_6$, is precipitated, whilst $\mathbf{Co}Cl_2$ remains in solution, thus:—

$$3\mathbf{Co}Ho_2 + Cl_2 = \underset{\substack{\text{Cobaltic}\\\text{hydrate.}}}{\mathbf{Co}_2Ho_6} + \mathbf{Co}Cl_2.$$

In the presence of an alkali (NaHo) the whole of the cobaltous hydrate is converted into $\mathbf{Co}_2Ho_6$.

AmHo produces in neutral solutions a slight precipitate of a **basic salt,** which dissolves readily in excess. The solution is reddish brown. Ammonic chloride prevents the precipitation altogether. The solution absorbs oxygen from the air, and becomes rapidly brown.

$CONao_2$ precipitates a *peach coloured* **basic carbonate,**

$COAmo_2$, same precipitate; readily soluble, however, in excess, to a red solution.

KCy gives with all normal cobaltous salts a *reddish brown* precipitate of **cobaltous cyanide,** $\mathbf{Co}Cy_2$, soluble in excess, reprecipitated by dilute hydrochloric or sulphuric acid.

If the cobaltous solution, however, contain free acid, so as to liberate hydrocyanic acid by the action of the latter upon the excess of KCy; and if the solution of $2KCy,\mathbf{Co}Cy_2$ be heated for some time, dilute hydrochloric or sulphuric acid no longer produces a precipitate, the whole of the cobaltous cyanide having been converted into cobaltic cyanide, $'\mathbf{Co}'''_2Cy_6$, which remains combined with 6KCy to form a well defined and stable salt, called **potassic cobalticyanide,** $K_6Co_2Cy_{12}$, hydrogen being evolved, thus:—

$$2\mathbf{Co}Cy_2 + 2HCy = \mathbf{Co}_2Cy_6 + H_2.$$

$$6KCy + \mathbf{Co}_2Cy_6 = \underset{\substack{\text{Potassic}\\\text{cobalticyanide.}}}{K_6Co_2Cy_{12}}.$$

which is not decomposed by dilute acids, nor by sodic hypochlorite in the cold.

Separation of Nickel from Cobalt.

It is obvious that the hydrocyanic acid reaction enables us to separate Ni from Co.—To a *neutral* solution of the two salts add cautiously a small quantity of a strong solution of HCy (a solution of potassic cyanide may likewise be used), and then, drop by drop, KHo, as long as a precipitate forms, and till the precipitate is quite redissolved. Heat gently for some time in a well ventilated closet, till the odour of HCy has disappeared. Allow to cool, and add a concentrated solution of ClNao. $\mathbf{Ni}_2Ho_6$ is precipitated in the cold, and cobalt remains in solution, as $K_6Co_2Cy_{12}$. Separate by filtration. Test the residue before the blowpipe for Ni, and evaporate the solution to dryness, and test for Co by means of a borax bead.

Instead of separating Ni as $\mathbf{Ni}_2Ho_6$ by means of ClNao, the solution, after boiling with excess of HCy, may also be precipitated whilst hot, with finely divided freshly precipitated **mercuric oxide**. On digesting for a short time at a gentle heat, the whole of the Ni is precipitated, partly as $\mathbf{Ni}Ho_2$, partly as $\mathbf{Ni}Cy_2$, the mercury combining with the liberated cyanogen. Filter off the *greenish* or *yellowish grey* precipitate, wash, and ignite. Pure $\mathbf{Ni}O$ is left; thus :—

$$(1)\ 2\mathbf{Ni}Cy_2 + x\mathbf{Hg}O = \mathbf{Hg}Cy_2 + \underset{\text{Greenish precipitate.}}{\mathbf{Ni}Ho_2,\mathbf{Ni}Cy_2} + x-1\mathbf{Hg}O.$$

$$(2)\ \mathbf{Ni}Ho_2,\mathbf{Ni}Cy_2 + \underset{\text{Excess.}}{\mathbf{Hg}O} = 2\mathbf{Ni}O + \underset{\text{Volatile on ignition.}}{\mathbf{Hg}Cy_2} + \mathbf{O}H_2.$$

The cobalt remains in the solution as $K_6Co_2Cy_{12}$. Nearly neutralize with dilute nitric acid, and add a neutral solution of mercurous nitrate, $\mathbf{N}_2O_4Hg_2o''$. A white precipitate of **mercurous cobalticyanide** $(Hg''_2)_3Co_2Cy_{12}$, forms, which contains the whole of the cobalt. Filter, wash, and ignite under a hood with free access of air, when **tricobaltic tetroxide**, $\mathbf{Co}_3O_4$, is left.

Add $\mathbf{N}OKo$ (**potassic nitrite**) in considerable excess to a concentrated normal solution of a cobaltous salt, then acetic acid in sufficient quantity to freely redissolve the precipitate, which is at first produced by the free KHo and $\mathbf{C}OKo_2$ contained in the $\mathbf{N}OKo$. On keeping the solution in a moderately warm place, all the cobalt separates in the form of a crystalline precipitate of a *fine yellow* colour (from a dilute solution only after long standing), the formation of which is expressed by the equation :—

$$2\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Coo'' + 12\mathbf{N}OKo + 2\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right. + \mathbf{O}H_2 = \underset{\text{Yellow}}{\mathbf{Co}_2O_3,3K_2O,}$$

$$\underset{\text{precipitate.}}{5N_2O_3,2\mathbf{O}H_2} + 4\mathbf{N}O_2Ko + 2\left\{\begin{matrix}\mathbf{C}H_3{}'\\ \mathbf{C}OKo\end{matrix}\right. + \mathbf{N}_2O_2.$$

The precipitate is soluble in much water; it is decomposed by hot nitric or hydrochloric acid, or by potassic hydrate; insoluble in alcohol; insoluble in the presence of potassic salts; and it can therefore be washed by a solution of potassic acetate, and finally with alcohol. THIS REACTION SERVES LIKEWISE FOR THE SEPARATION OF NICKEL FROM COBALT.

On igniting a small quantity of $\mathbf{N}_2O_4Nio''$, a dirty greyish powder of $\mathbf{Ni}O$ is left. Ignite next $\mathbf{N}_2O_4Coo''$ gently, and a black residue of cobaltous dicobaltic tetroxide, $\mathbf{Co}_3O_4 = \left\{\begin{matrix}\mathbf{Co}O\\ \mathbf{Co}O\end{matrix}\right.Coo''$ is left. On treating this oxide with hydrochloric acid, chlorine gas is evolved, according to the equation :—

$$\mathbf{Co}_3O_4 + 8HCl = 3\mathbf{Co}Cl_2 + Cl_2 + 4\mathbf{O}H_2.$$

Both nickel and cobalt are capable of forming compounds in which the metals exist in a **tetrad** condition, viz.,

$$\mathbf{Ni}_2O_3, \text{ or } \underset{\text{Nickelic oxide.}}{\left\{\begin{matrix}\mathbf{Ni}O\\ \mathbf{Ni}O\end{matrix}\right.O}, \text{ and } \mathbf{Co}_2O_3, \text{ or } \underset{\text{Cobaltic oxide.}}{\left\{\begin{matrix}\mathbf{Co}O\\ \mathbf{Co}O\end{matrix}\right.O}; \underset{\text{Cobaltic sulphide.}}{\mathbf{Co}_2S_3}$$

$\mathbf{Ni}_2O_3$ is, however, obtained in the wet way only, and cannot exist at a high temperature.

$\mathbf{Co}_3O_4$, on the other hand, is obtained in the dry way, or on gentle ignition, giving up a portion of its oxygen only on strong ignition.

The same tendency to form compounds in which nickel and cobalt exist as tetrad elements, is observed on exposing their alkaline solutions to the air, or on passing chlorine or adding bromine or iodine to their solutions.

Little use is, however, made of these reactions beyond the conversion of $\mathbf{Co}Cy_2$ into $\mathbf{Co}_2Cy_6$, in the presence of potassic cyanide, or of $\mathbf{Co}O$ into $\mathbf{Co}_2O_3$ in the potassic nitrite reaction.

QUESTIONS AND EXERCISES.

1. Translate into graphic formulæ the constitutional formulæ of *cobalt pyrites*, *cobalt vitriol*, *cobalt bloom*, cobaltic cyanide.
2. How are $\mathbf{Co}O$ and $\mathbf{Co}_3O_4$ prepared?
3. How is Co separated from Ni?
4. 2 grms. of an ore containing Ni and Co yield ·221 grm. of $\mathbf{Ni}O$ and ·1575 grm. of $\mathbf{Co}_3O_4$, what is the percentage of Ni and Co in the ore?
5. Explain the formation of a blue glass when cobalt compounds are heated in a borax bead, or a bead of microcosmic salt.
6. How would you prepare potassic cobalticyanide?

MANGANESE, Mn'', ^{iv}, and ^{vi}.—Occurs in nature mainly in the state of OXIDES, of which the mineral *pyrolusite*, $\mathbf{Mn}^{iv}O_2$, is the most important. It is found in small quantities in many iron ores, and is a frequent constituent of SILICATES: the $\mathbf{Mn}O$ replacing the isomorphous bases $\mathbf{Fe}O$, $\mathbf{Zn}O$, $\mathbf{Mg}O$, $\mathbf{Ca}O$, without altering the crystalline structure of the minerals. It exists both in the dyad and tetrad condition in manganous and manganic oxides. The ANHYDROUS OXIDES known, besides pyrolusite, are: *braunite*, $\mathbf{Mn}^{iv}{}_2O_3$, *hausmannite*, $\mathbf{Mn}^{iv}{}_3O_4$; the HYDRATES are: *manganite*, $\left\{\begin{matrix}\mathbf{Mn}OHo\\ \mathbf{Mn}OHo\end{matrix}\right.$, *psilomelane*, $\begin{matrix}\mathbf{Mn}Ho\\ \mathbf{Mn}Ho\end{matrix}O_2Mno''$, *Wad*, $\begin{matrix}\mathbf{Mn}Ho_3\\ \mathbf{Mn}Ho_3\end{matrix}Mno''$, *Varvicite*, $\left\{\begin{matrix}{}'\mathbf{Mn}'''O\text{-}O\\ Mno''\\ {}'\mathbf{Mn}'''O\text{-}O\end{matrix}\right]\ (Mn^{iv}Ho_2)''$, *copper mangan*, $\begin{matrix}\mathbf{Mn}Ho_2\\ \mathbf{Mn}Ho_2\end{matrix}OCuo''$. Manganese is found in combination with SULPHUR, in *manganese blende*, $\mathbf{Mn}S$; with CARBONIC ACID, in *diallogite*, $\mathbf{C}OMno''$; with SILICA, in *red manganese or mangan kiesel (rhodonite)*, $\mathbf{Si}OMno''$,and in *tephroite*, $\mathbf{Si}Mno''_2$; with PHOSPHORIC acid, as *triplite*, $\mathbf{P}_2OMno''_4$, $\mathbf{P}_2OFeo''_4$.

EXAMINATION IN THE DRY WAY.

The presence of manganese is readily detected in minerals which contain no other oxides, capable of colouring fluxes; as it imparts to the *borax* bead, or to a bead of microcosmic salt, a fine **amethyst** colour when heated in the *outer* flame, and the bead becomes **colourless** when heated in the *reducing* flame. If other metallic oxides are present, it is preferable to mix a portion of the finely powdered mineral with two or three times its weight of $\mathbf{C}ONao_2$ (a little nitre may likewise be added), and to fuse on platinum foil (a small platinum spoon or the lid of a platinum crucible) in the oxidizing flame, when a **bluish green mass**, consisting of **sodic manganate**, $\mathbf{Mn}O_2Nao_2$, is left. THIS FORMS THE MOST CHARACTERISTIC REACTION FOR MANGANESE. Manganous and manganic oxides are converted into a higher oxide, $\mathbf{Mn}^{vi}O_3$, in which Mn exists as a hexad.

EXAMINATION IN THE WET WAY.

All the higher oxides of manganese, when heated with hydrochloric acid, evolve chlorine, and are converted into manganous chloride, $\mathbf{Mn}Cl_2$:—the chlorine so evolved becomes the measure of the amount of $\mathbf{Mn}O_2$ present in a manganese ore.

We employ A SOLUTION OF MANGANOUS CHLORIDE, $\mathbf{Mn}Cl_2$ (free from Fe).

$\mathbf{S}Am_2$ (**group-reagent**) gives a *flesh-coloured* precipitate of **manganous sulphide**, $\mathbf{Mn}S$, readily soluble in dilute acids, even acetic acid. Hence the presence of free acetic acid prevents the precipitation of manganese (METHOD OF DISTINGUISHING CO AND NI FROM MN). The manganese may be separated by repeating once or twice the precipitation of cobalt and nickel in the presence of acetic acid.

$\mathbf{S}H_2$ does not precipitate a neutral solution of a manganous salt; the acetate even is precipitated very slowly and imperfectly, and not at all when free acetic acid is present.

KHo or NaHo gives a *white* precipitate of **manganous hydrate**, $\mathbf{Mn}Ho_2$, insoluble in excess. The precipitate absorbs speedily oxygen from the air, and turns dark brown with formation of $\left\{\begin{matrix}\mathbf{Mn}OHo\\ \mathbf{Mn}OHo\end{matrix}\right.$, when it no longer dissolves completely in ammonic chloride.

AmHo precipitates a *white hydrate*, $\mathbf{Mn}Ho_2$, from neutral solutions; insoluble in excess, or in ammonic carbonate.

No precipitate is produced in solutions containing ammonic chloride. On exposing an ammoniacal solution of the soluble double chloride, $2AmCl,\mathbf{Mn}Cl_2$, to the action of the air, the whole of the manganese is gradually precipitated as brown **dimanganic dioxydihydrate**, $\left\{\begin{matrix}\mathbf{Mn}OHo\\ \mathbf{Mn}OHo\end{matrix}\right.$. This reaction is characteristic for manganese compounds.

AmHo conveys in this change oxygen to the manganous salt in a manner similar to the action it had upon cobaltous salts, and upon metallic copper, in the presence of oxygen or air (comp. p. 128); forming, however, in the case of the manganese compound, an insoluble body.

Owing to this tendency of manganous salts to become oxidized and precipitated in the presence of AmHo, it is impossible to separate manganous from ferric salts by means of AmCl and AmHo. The reddish brown ferric hydrate, which is precipitated, invariably carries down more or less $\left\{\begin{matrix}\mathbf{Mn}OHo\\ \mathbf{Mn}OHo\end{matrix}\right.$; and *small quantities of manganese cannot, therefore, be separated from iron by precipitation with AmCl and AmHo.*

$\mathbf{C}ONao_2$ or $\mathbf{C}OKo_2$ precipitates *white* **manganous carbonate**, $\mathbf{C}OMno''$, insoluble in excess of the reagent, but pretty readily soluble in ammonic chloride. This precipitate absorbs likewise oxygen from the air, and turns to a dirty brownish white colour, owing to the formation of dimanganic dioxydihydrate. On ignition with free access of air, the white carbonate turns first black, and changes subsequently to brown **trimanganic tetroxide**, $\mathbf{Mn}_3O_4$. All manganese oxides are obtained upon ignition in air in the form of $\mathbf{Mn}_3O_4$.

KCy gives a *whitish* precipitate of **manganous cyanide**, $\mathbf{Mn}Cy_2$, soluble in excess to a brown solution, which is not precipitated by $\mathbf{S}Am_2$.

We have just seen how readily manganous compounds are converted, more or less completely, into higher oxides, in which Mn acts the part of a tetrad element. In the brown hydrated dioxide, $\mathbf{Mn}^{iv}OHo_2$, obtained when a manganous salt is digested with sodic hypochlorite, according to the equation:—

$$\mathbf{Mn}Cl_2 + ClNao + 2\mathbf{O}H_2 = \mathbf{Mn}^{iv}OHo_2 + NaCl + 2HCl,$$

the manganese exists likewise as a tetrad element. By fusion in the dry way with $\mathbf{C}ONao_2$, alone or together with nitre, the manganous or manganic compounds are converted into an alkaline manganate, $\mathbf{Mn}^{vi}O_2Nao_2$, in which the metal manganese acts the part of a hexad element. Manganic acid itself has never been isolated. It is obtained, however, in combination with a few of the stronger metallic bases, forming manganates, of which the alkaline manganates only dissolve in water to *green solutions*.

Manganates are readily decomposed in aqueous solutions. On gently heating a solution of potassic manganate with free access of air, the green colour changes to *purple red*, owing to the formation of potassic permanganate,* $\mathbf{Mn}_2O_6Ko_2 = \left\{\begin{matrix} '\mathbf{Mn}^{v}O_2(OKo) \\ '\mathbf{Mn}^{v}O_2(OKo) \end{matrix}\right.$ with separation of $\mathbf{Mn}^{iv}OHo_2$, thus:—

$$3\mathbf{Mn}O_2Ko_2 + 3\mathbf{O}H_2 = \mathbf{Mn}_2O_6Ko_2 + \mathbf{Mn}OHo_2 + 4KHo.$$

The change is accelerated by adding a few drops of a dilute mineral acid (*e.g.*, nitric, hydrochloric or sulphuric acid), which combines with the liberated alkali. This reaction is extremely delicate.

The metal manganese seems to act here the part of a pseudo-octad element; and it may readily be inferred that the different oxygen atoms perform different functions in such a highly oxygenized compound, and that the metal manganese will part with some more readily than with others.

Manganic oxide, $\mathbf{Mn}^{iv}O_2$, as well as other native peroxides, already enumerated, also the alkaline manganates and permanganates, act as powerful oxidisers, differing merely in the *intensity* of their oxidizing action.

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* Permanganic acid has never been isolated. It exists only in a few metallic salts called *permanganates*, which are soluble in water forming intensely purple-red solutions. The salts crystallise from an alkaline solution in beautiful large crystals of deep violet lustre.

Manganic oxide gives off oxygen on the addition of sulphuric acid, and forms normal manganous sulphate:—

$$\text{(Atomic equation) } \mathbf{Mn}O_2 + \mathbf{S}O_2Ho_2 = O + \mathbf{S}O_2Mno'' + \mathbf{O}H_2.$$

Sulphuric acid added to $\mathbf{Mn}O_2Nao_2$, gives off a molecule of oxygen and forms manganous and sodic sulphates, thus:—

$$\mathbf{Mn}O_2Nao_2 + 2\mathbf{S}O_2Ho_2 = O_2 + \mathbf{S}O_2Mno'' + \mathbf{S}O_2Nao_2 + 2\mathbf{O}H_2.$$

Sulphuric acid added to a solution of $\left\{\begin{matrix}\mathbf{Mn}O_3(OKo)\\ \mathbf{Mn}O_3(OKo)\end{matrix}\right.$, liberates five atoms of oxygen, and leaves manganous and potassic sulphates in the solution, thus:—

$$\text{(Atomic equation) } \left\{\begin{matrix}\mathbf{Mn}O_3(OKo)\\ \mathbf{Mn}O_3(OKo)\end{matrix}\right. + 3\mathbf{S}O_2Ho_2 = O_5 + 2\mathbf{S}O_2Mno'' + \mathbf{S}O_2Ko_2 + 3\mathbf{O}H_2.$$

Hydrochloric acid acts likewise upon the higher oxides of manganese with evolution of chlorine and formation of metallic chlorides and water. The peroxides of manganese, especially the *black oxide*, constitute the principal substances, together with hydrochloric acid, for evolving chlorine in the laboratory and on a manufacturing scale.

We know of no other mineral oxidizing agent capable of yielding from one molecular group of elements five atoms of oxygen; and there are but few elementary substances which resist the oxidizing action of potassic permanganate. Hydrogen, freshly-ignited carbon, phosphorus, iodine, sulphuretted hydrogen, carbonic disulphide, are oxidized more or less rapidly. Metals, such as zinc and iron, become oxidized after a few days; lead, copper, mercury and silver after some time. Many lower oxides, chlorides, etc., are converted into higher oxides, etc., for example:—

$\mathbf{As}Ho_3$ Arsenious acid.	is converted into	$\mathbf{As}OHo_3$ Arsenic acid.
$\mathbf{S}OHo_2$ Sulphurous acid.	„	$\mathbf{S}O_2Ho_2$. Sulphuric acid.
$\mathbf{N}OHo$ Nitrous acid.	„	$\mathbf{N}O_2Ho$. Nitric acid.
$\mathbf{P}OHHo_2$ Phosphorous acid.	„	$\mathbf{P}OHo_3$. Phosphoric acid.

$\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right.$ is converted into $2\mathbf{C}O_2 + \mathbf{O}H_2$.
Oxalic acid.

$2\mathbf{Fe}Cl_2$ Ferrous chloride.	„	$\mathbf{Fe}_2Cl_6$ Ferric chloride.	(in presence of dilute HCl).
$\mathbf{Sn}Cl_2$ Stannous chloride.	„	$\mathbf{Sn}Cl_4$ Stannic chloride.	„
$\mathbf{Sb}Cl_3$ Antimonious chloride.	„	$\mathbf{Sb}Cl_5$ Antimonic chloride.	„
$\mathbf{Cu}_2Cl_2$ Cuprous chloride.	„	$2\mathbf{Cu}Cl_2$ Cupric chloride.	„
$\mathbf{Hg}_2Cl_2$ Mercurous chloride.	„	$2\mathbf{Hg}Cl_2$ Mercuric chloride.	„
$2\mathbf{S}O_2Feo''$ Ferrous sulphate.	„	$\mathbf{S}_2O_6Fe_2o^{vi}$ Ferric sulphate.	(in presence of dilute $\mathbf{S}O_2Ho_2$).

Potassic permanganate oxidizes many organic bodies, such as sugar, gum, cellulose (in paper, cotton), uric acid, etc. The reaction is indicated by a change of colour; on adding, for instance, the purple coloured solution to a solution of $\mathbf{S}OHo_2$, the colour is instantaneously destroyed as long as any $\mathbf{S}OHo_2$ is left. Permanganate becomes, therefore, the measure for sulphurous acid, and in like manner for other lower oxides, chlorides, etc.

$\mathbf{S}OHo_2$ requires one atom of oxygen in order to be converted into $\mathbf{S}O_2Ho_2$, and $\mathbf{Mn}_2O_6Ko_2$ can part with five atoms of oxygen. One molecule of the oxidizing agent oxidizes, therefore, five molecules of the reducing agent, *i.e.*, 316 parts by weight of $\mathbf{Mn}_2O_6Ko_2$ become the measure for $5 \times 64 = 320$ parts by weight of $\mathbf{S}O_2$.

Two molecules of $\mathbf{S}O_2Feo''$ combine with one atom of oxygen and one molecule of $\mathbf{S}O_2Ho_2$, to form one molecule of ferric sulphate, thus:—

$$2\mathbf{S}O_2Feo'' + O + \mathbf{S}O_2Ho_2 = \mathbf{S}_2O_6Fe_2o^{vi} + \mathbf{O}H_2.$$

Hence one molecule of dipotassic permanganate oxidizes ten molecules of $\mathbf{S}O_2Feo''$, ten molecules of $\mathbf{Fe}O$, or ten atoms of Fe; and 316 parts by weight of $\mathbf{Mn}_2O_6Ko_2$ become the measure for

10×152 parts by weight of $\mathbf{S}O_2Feo''$
or 10×72 „ $\mathbf{Fe}O$
or 10×56 „ Fe.

QUESTIONS AND EXERCISES.

1. Which are the most important manganese ores?
2. Which manganese ores can be employed for generating chlorine?
3. Explain the action of $\mathbf{S}O_2Ho_2$ upon $\mathbf{Mn}O_2$, $\mathbf{Mn}O_2NaO_2$ and $\mathbf{Mn}_2O_6Ko_2$; and express the changes by equations.
4. Translate into graphic formulæ the constitutional formulæ of *pyrolusite*, *braunite*, *hausmannite*, *manganite*, *psilomelane*, *wad*, *varvicite*, and *tephroite*.
5. Describe the most characteristic blowpipe reactions for manganese compounds.
6. How can Mn be separated from Ni and Co?
7. How is Mn separated from calcium or from potassium?
8. What change does a solution of $\mathbf{Mn}O_2Ko_2$ undergo when heated in contact with air?
9. Give evidences of the dyad, tetrad and hexad nature of manganese.
10. Give the graphic formulæ for disodic manganate and dipotassic permanganate?
11. Explain the action of AmHo upon cobaltous and manganous salts, 1st, in the presence of ammonic chloride; 2nd, in the absence of ammonic salts; and 3rd, with free access of air.
12. State why Mn is separated with difficulty from Fe^{iv} by means of AmCl and AmHo.
13. What change does $\mathbf{C}OMno''$ undergo upon ignition?
14. By precipitating 2·622 grms. of a manganous salt with $\mathbf{C}ONao_2$ and ignition of the precipitate, 1·325 grm. of $\mathbf{Mn}_3O_4$ are left; what is the percentage of manganese in the salt?
15. Give an account of how chlorine is prepared on a manufacturing scale.
16. Why does dipotassic permanganate act as a powerful oxidizing agent?
17. What is the action of dipotassic permanganate upon HCl, $\mathbf{S}H_2$, $\mathbf{S}O_2$, $\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right.$, $\mathbf{Cu}_2Cl_2$, $\mathbf{Fe}Cl_2$, $\mathbf{Sn}Cl_2$? Express the changes by equations.
18. How much gaseous $\mathbf{S}O_2$ by weight and by volume (at 0° C. and 760 mm. barometrical pressure) will be required to decolourize a solution containing ·500 grm. of dipotassic permanganate?
19. Explain the action of $\mathbf{S}O_2$ upon manganic dioxide.
20. ·125 grm. of dipotassic permanganate had to be added to a given quantity of an acid ($\mathbf{S}O_2Ho_2$) solution of $\mathbf{S}O_2Feo''$. Calculate how much metallic iron the solution contained.
21. ·450 grm. of *spathic iron ore*, $\mathbf{C}OFeo''$, when dissolved in hydrochloric acid, required ·100 grm. of $\mathbf{Mn}_2O_6Ko_2$. What will be the percentage—1st, of carbonate; 2nd, of metallic iron, contained in the ore?
22. 1·240 grm. of $\mathbf{C}O_2$ was evolved when 1·780 grm. of *pyrolusite* was treated with moderately concentrated $\mathbf{S}O_2Ho_2$ and $\left\{\begin{matrix}\mathbf{C}OKo\\ \mathbf{C}OKo\end{matrix}\right.$. What is the percentage of $\mathbf{Mn}O_2$ in the ore, and how much chlorine gas by weight and by volume can be evolved from 100 grms. of the ore when treated with HCl?

ZINC, Zn''.—Occurs in nature chiefly as SULPHIDE, or *zinc blende*, *black-jack*, $\mathbf{Zn}S$; as CARBONATE, or *calamine*, $\mathbf{C}OZno''$; and as SILICATE, or *zinc glance*, *electric calamine*, $\mathbf{Si}Zno''_2,\mathbf{O}H_2$, *Willemite*, $\mathbf{Si}Zno''_2$*; also as OXIDE, in *red zinc ore*, $\mathbf{Zn}O$.

REACTIONS IN THE DRY WAY.

The most characteristic blowpipe reaction for zinc consists in the white incrustation of zincic oxide, $\mathbf{Zn}O$, which its compounds yield when heated on charcoal in the reducing flame with $\mathbf{C}ONao_2$. The zinc compound is reduced to the metallic state, and the metal being volatile, burns on passing through the outer flame, with a bluish green flame, and is converted into oxide, which covers the charcoal with an incrustation, **yellow** when hot, **white** when cold, and which assumes a **fine green** colour when treated with a solution of cobaltous nitrate, and on being once more strongly heated in the outer flame. The incrustation is not driven away in the oxidizing flame,—$\mathbf{Zn}O$ being non-volatile.

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* Naumann's Elements of Mineralogy.

Zinc compounds give with borax or microcosmic salt in both flames a bead, which is yellowish while hot, and white on cooling; opaque if much zinc salt be present. This applies, however, only to pure zinc compounds, and the detection of zinc in poor ores containing other readily oxidizable metals (such as Pb, Cd, As, Sb, which give likewise incrustations), is a matter of great uncertainty.

Zincic sulphide, $\mathbf{Zn}S$ (*zinc blende*), when roasted in a tube of hard glass, loses part of its sulphur in the form of sulphurous anhydride, and leaves some zincic sulphate, $\mathbf{S}O_2Zno''$ (*white vitriol*), which may be extracted with water.

Calamine, $\mathbf{C}OZno''$, leaves on ignition zincic oxide, $\mathbf{Zn}O$.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF ZINCIC CHLORIDE, $\mathbf{Zn}Cl_2$, OR OF ZINCIC SULPHATE, $\mathbf{S}O_2Zno''$.

$\mathbf{S}Am_2$ **(group-reagent)** gives a *white* precipitate of **zincic sulphide**, $\mathbf{Zn}S$, insoluble in excess. From dilute solutions the $\mathbf{Zn}S$ separates only after some time. It is readily decomposed by dilute hydrochloric and sulphuric acids, with evolution of sulphuretted hydrogen; also by nitric acid, but is insoluble in acetic acid.

$\mathbf{S}H_2$ precipitates zinc imperfectly from neutral solutions of zincic salts with mineral acids; but from an acetate or a solution of a zincic salt mixed with an alkaline acetate, the whole of the metal is precipitated by $\mathbf{S}H_2$ as $\mathbf{Zn}S$, even in the presence of much acetic acid (METHOD OF SEPARATION OF ZN FROM MN). Free organic acids prevent the precipitation.

KHo or NaHo precipitates the *white* **hydrate**, $\mathbf{Zn}Ho_2$, readily soluble in excess, and in AmHo, reprecipitated on diluting with water and on boiling; soluble also in ammonic chloride. $\mathbf{S}H_2$ precipitates the whole of the zinc from these solutions. Free organic acids prevent the complete precipitation. In the presence of manganese, nickel and cobalt, KHo or NaHo does not dissolve out the whole of the zincic hydrate.

$\mathbf{C}ONao_2$ or $\mathbf{C}OKo_2$ produces a *white* precipitate of **basic carbonate**, consisting of two molecules of zincic carbonate and three molecules of zincic hydrate, according to the equation:—

$$5\mathbf{S}O_2Zno'' + 5\mathbf{C}ONao_2 + 3\mathbf{O}H_2 = \left\{\begin{array}{l}\mathbf{C}Ho(OZn''Ho)_2\\ Zno''\\ \mathbf{C}Ho(OZn''Ho)_2\end{array}\right. + 5\mathbf{S}O_2Nao_2$$

Dihydric pentazincic dicarbonate tetrahydrate.

$$+\ 3\mathbf{C}O_2.$$

This carbonate leaves on ignition $\mathbf{Zn}O$, also known under the name of *zinc white*.

$\mathbf{C}OAmo_2$ produces the same precipitate, soluble, however, in excess.

KCy gives a *white* precipitate of **zincic cyanide**, $\mathbf{Zn}Cy_2$; soluble in excess, not reprecipitated by $\mathbf{S}Am_2$, but completely precipitated by $\mathbf{S}K_2$ as $\mathbf{Zn}S$ (Method for the separation of Zn from Ni).

Zinc precipitates the less electropositive metals from their solutions, viz., As, Sb, Sn, Cd, Cu, Pb, Ag, Bi, Hg: and on dissolving impure metallic zinc in dilute acids (hydrochloric or sulphuric), these metals do not dissolve, as long as any zinc remains undissolved. Hence zinc protects other metals, such as copper, iron (galvanized iron), from the oxidizing action of the air.

Zinc, when placed in contact with platinum, iron, etc., dissolves in alkaline solutions in the cold; when boiled with KHo ($NaHo$, or even $AmHo$), it dissolves likewise, with evolution of hydrogen and formation of **dipotassic zincic oxide**, $\mathbf{Zn}Ko_2$.

Zinc vapour decomposes $\mathbf{C}O_2$ at a high temperature, and forms $\mathbf{Zn}O$ and $\mathbf{C}O$; at a lower temperature, $\mathbf{Zn}O$ yields its oxygen again to carbon (Method of extracting metallic zinc from some of its ores). This forms another interesting instance of reciprocal chemical action.

QUESTIONS AND EXERCISES.

1. Explain the action of HCl, $\mathbf{S}O_2Ho_2$, $\mathbf{N}O_2Ho$, and KHo upon metallic zinc. Express the changes by equations.
2. Give the names and composition of the most important zinc ores, and translate their constitutional into graphic formulæ.
3. Describe the blowpipe reactions for zinc compounds.
4. Express by equations the reactions for zinc in the wet way. Give graphic formulæ for the basic carbonate and dipotassic zincic oxide.
5. 1·5 grm. of *calamine* yielded ·876 grm. of ZnO, what is the percentage of zinc in the ore?
6. How is metallic zinc obtained from *calamine* or *red zinc ore?*
7. How has $\mathbf{Zn}S$ to be treated in order to extract from it metallic zinc?
8. How is Zn separated from Mn?
9. How can Zn be separated from Ni and Co?
10. How would you remove the zinc from an alloy of Zn and Cu (brass)?
11. How is *white vitriol* prepared, 1st, from *zinc blende*, 2nd, from *calamine?* Give the composition of the crystallised salt.
12. You have given to you *calamine*, *zinc blende*, hydrochloric acid, water, and sodic carbonate. State how you would prepare from these materials zincic oxide or *zinc white*. Express the changes by equations.

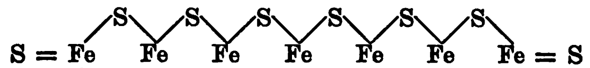
IRON. Fe'', ^{iv} and ^{vi}.—One of the few metallic elements which occurs very abundantly in nature, both in the free and combined state. It will suffice if we consider more especially those iron ores which contain the metal in sufficient quantities and which are sufficiently free from deleterious substances (such as S, P, As), to render them suitable for the extraction of iron by the usual metallurgical processes. The most important iron ores are:—

1st. ORES CONTAINING FERROUS OXIDE:—*spathic* or *sparry iron ore*, $\mathbf{C}OFeo''$ (*sphaerosiderite*), containing varying quantities of $\mathbf{C}OMno''$, $\mathbf{C}OMgo''$, and $\mathbf{C}OCao''$; *black band* or carbonaceous iron ore, a sphaerosiderite containing from 20 to 25 per cent. of bituminous matter; *clay ironstone* (likewise a sideride) is, as its name indicates, associated with clayey matter. It is from these two ores that the greater part of the iron manufactured in this country is derived. They occur in the immediate proximity to the coal measures and limestone beds—the fuel and flux necessary for their reduction to the metallic state.

2nd. ORES CONTAINING FERROUS AND FERRIC OXIDES: *viz.*, *magnetic iron ore*, $\left\{\begin{matrix}\mathbf{Fe}\mathrm{O}\\ \mathbf{Fe}\mathrm{O}\end{matrix}\right.\mathrm{Feo}''$ (ferrous diferric tetroxide).

3rd. ORES CONTAINING FERRIC OXIDE ONLY: *viz.*, *red hæmatite* (*micaceous iron*, *oligist*, *specular iron* or *iron glance*), $'\mathbf{Fe}'''_2\mathrm{O}_3 = \left\{\begin{matrix}\mathbf{Fe}\mathrm{O}\\ \mathbf{Fe}\mathrm{O}\end{matrix}\right.\mathrm{O}$ (ferric oxide). This oxide forms different hydrates which, according to the amount of water which they contain, have received different names, viz., *turgite*, $2\mathbf{Fe}_2\mathrm{O}_3, \mathbf{O}\mathrm{H}_2 = \left\{\begin{array}{l}\mathbf{Fe}\mathrm{OHo}\\ \begin{matrix}\mathbf{Fe}\mathrm{O}\\ \mathbf{Fe}\mathrm{O}\end{matrix}\mathrm{O}\\ \mathbf{Fe}\mathrm{OHo}\end{array}\right.$ (tetraferric pentoxy-dihydrate); *needle iron ore*, *brown iron ore* or *pyrrhosiderite*, $\mathbf{Fe}_2\mathrm{O}_3, \mathbf{O}\mathrm{H}_2 = \left\{\begin{matrix}\mathbf{Fe}\mathrm{OHo}\\ \mathbf{Fe}\mathrm{OHo}\end{matrix}\right.$ (diferric dioxy-dihydrate); *limonite* or compact *brown iron ore*, *brown hæmatite*, $2\mathbf{Fe}_2\mathrm{O}_3, 3\mathbf{O}\mathrm{H}_2 = \left\{\begin{array}{l}\mathbf{Fe}\mathrm{OHo}\\ \mathbf{Fe}\mathrm{Ho}_2\\ \mathrm{O}\\ \mathbf{Fe}\mathrm{Ho}_2\\ \mathbf{Fe}\mathrm{OHo}\end{array}\right.$ (tetraferric trioxy-hexahydrate); (varieties: *oolitic iron ore*, *pea ore*); *yellow iron ore* or *xanthosiderite*, $\mathbf{Fe}_2\mathrm{O}_3, 2\mathbf{O}\mathrm{H}_2 = \left\{\begin{matrix}\mathbf{Fe}\mathrm{Ho}_2\\ \mathbf{Fe}\mathrm{Ho}_2\end{matrix}\right.\mathrm{O}$ (diferric oxy-tetrahydrate).

A few other iron ores deserve our attention. They are not used for the extraction of iron, but are valuable as a cheap source of sulphur, viz., *iron pyrites*, *martial pyrites*, or *mundic*, $\mathbf{Fe}\mathrm{S}_2$, found abundantly in nature; $\mathbf{Fe}_2\mathrm{S}_3$, (diferric trisulphide); *copper pyrites*, $\left\{\begin{matrix}\mathbf{Fe}\mathrm{S}\\ \mathbf{Fe}\mathrm{S}\end{matrix}\right.\mathrm{Cu_2s}''$, and *magnetic pyrites*, $5\mathbf{Fe}\mathrm{S}, \mathbf{Fe}_2\mathrm{S}_3 = \mathbf{Fe}_7\mathrm{S}_8$, which may be expressed graphically, thus:—



(Penta-ferrous diferric octasulphide).

Besides these ores, iron is found in nature in combination with ARSENIC and SULPHUR, in *mispickel* $\begin{matrix}''\mathbf{As}'\\ ''\mathbf{As}'\end{matrix}\mathrm{Fe,Fe^{iv}S_2}$; with CHROMIUM as *chrome iron ore* $\left\{\begin{matrix}'\mathbf{Cr}'''\mathrm{O}\\ '\mathbf{Cr}'''\mathrm{O}\end{matrix}\right.\mathrm{Feo}''$; with SILICA as *chloropal*, $\begin{array}{l}\mathbf{Si}\mathrm{O}\urcorner\\ \mathbf{Si}\mathrm{O}-\mathrm{Fe_2o^{vi}}\\ \mathbf{Si}\mathrm{O}\lrcorner\end{array}$, $3\mathbf{O}\mathrm{H}_2$, and many other silicates; as SULPHATE, in *green copperas* or *green vitriol*, $\mathbf{S}\mathrm{OHo_2Feo}''$, $6\mathbf{O}\mathrm{H}_2$; as phosphate in *vivianite*,*

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* Contains also ferric phosphate, $\mathbf{P}_2\mathrm{O_2Fe_2o^{vi}}$, $8\mathbf{O}\mathrm{H}_2$, to which the blue colour of the mineral is due.

$\mathbf{P}_2O_2Feo''_3$, $8\mathbf{O}H_2$ (triferrous phosphate), and others; as ARSENIATE, in *scorodita*, $\mathbf{As}_2O_2Fe_2o^{vi}$, $4\mathbf{O}H_2$, and others.

REACTIONS IN THE DRY WAY.

On heating the different ferric compounds before the blowpipe, they turn black and become magnetic; when heated in the *outer* flame, on a *borax* bead, iron compounds impart a **dark red** colour to the borax, whilst hot, becoming **light yellow**, when cold. In the *reducing* flame they give an **olive green** to **bottle green** bead.

The reactions with microcosmic salt are similar but less distinct. The presence of Co, Cu, Ni, Cr conceals the colour of the iron bead. Ferric sulphides and arsenides must be roasted, previous to being introduced into the borax bead. When heated with $\mathbf{C}ONao_2$ on charcoal in the reducing flame, metallic iron is obtained as a magnetic powder.

REACTIONS IN THE WET WAY.

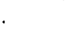
Iron forms two series of salts: viz., FERROUS AND FERRIC SALTS. It dissolves readily in dilute acids, such as HCl, $\mathbf{S}O_2Ho_2$, forming ferrous salts, $\mathbf{Fe}Cl_2$, $\mathbf{S}O_2Feo''$, with evolution of hydrogen. Cold dilute nitric acid dissolves finely divided iron (iron filings) without evolving hydrogen gas, the nitric acid being decomposed, so as to form ferrous nitrate and a small amount of ammonic nitrate, thus:—

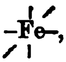
$$4Fe + 10\,\mathbf{N}O_2Ho = 4\left\{\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}\right.Feo'' + \mathbf{N}O_2Amo + 3\mathbf{O}H_2.$$

The metal iron exists in all these salts in the dyad condition, but exhibits a marked tendency to pass into the tetrad condition. Exposed to the air, $\mathbf{Fe}Cl_2$ and $\mathbf{S}O_2Feo''$ absorb oxygen and are gradually converted into ferric salts. The same change is produced by the action of various oxidizing agents, such as Cl_2, Br_2, I_2, ClNao, KO_3Cl in the presence of HCl, $\mathbf{N}O_2Ho$, $\mathbf{N}O_2Ago$, $\mathbf{Au}Cl_3$, $\mathbf{Hg}Cl_2$, $\mathbf{Mn}_2O_6Ko_2$, $\mathbf{Cr}O_2Ko_2$, and others. *We possess therefore in ferrous compounds powerful reducing agents.*

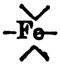
The tetrad condition appears to be the natural state of existence of the metal iron. This is rendered evident, moreover, by the limited number of ferrous compounds which exist in nature. The latter must be viewed as unsatisfied bodies, which, under favourable conditions, deprive other bodies directly or indirectly of oxygen, to form ferric compounds. Dyad iron, Fe'', (called *ferrosum*) has two bonds latent, which it is eager to satisfy, so as to become converted into the more stable tetrad iron, Fe^{iv} (or *ferricum*), in which condition it occurs in nature in combination with sulphur only, as $\mathbf{Fe}S_2$, without forming any corresponding oxygen, chlorine, etc., compounds. Two atoms of tetrad iron are invariably linked together in ferric oxide, chloride, etc., whereby iron becomes a pseudo-triad element. It is possible to combine, by artificial means, three atoms of oxygen with one atom of iron, so as to form ferrates, as in potassic ferrate, $\mathbf{Fe}O_2Ko_2$, in which compound the iron exists as a hexad element.

This condition of the metal iron may be represented graphically, hus:—

Dyad iron , *e.g.*, in $\mathbf{Fe}Cl_2$, $\mathbf{Fe}O$, $\mathbf{Fe}S$.

Tetrad iron , or pseudo-triad iron, $-\overset{|}{\underset{|}{\mathrm{Fe}}}-\overset{|}{\underset{|}{\mathrm{Fe}}}-$, *e.g.*, in

$\mathbf{Fe}S_2$, $\left\{\begin{matrix}'\mathbf{Fe}'''Cl_3\\'\mathbf{Fe}'''Cl_3'\end{matrix}\right.$ $\left\{\begin{matrix}'\mathbf{Fe}'''S\\'\mathbf{Fe}'''S\end{matrix}\right.S$, $\left\{\begin{matrix}'\mathbf{Fe}'''O\\'\mathbf{Fe}'''O\end{matrix}\right.O$, and lastly as

Hexad iron  or $=\underset{\|}{\mathrm{Fe}}=$ *e.g.*, in $\mathbf{Fe}^{vi}O_2Ko_2$.

A. Ferrous compounds.—We employ A SOLUTION OF FERROUS SULPHATE, $\mathbf{S}O_2Feo''$.

$\mathbf{S}Am_2$ (**group-reagent**) gives a *black* precipitate of **ferrous sulphide**, $\mathbf{Fe}S$, insoluble in alkalies and alkaline sulphides, decomposed by dilute hydrochloric acid with evolution of $\mathbf{S}H_2$. The moist precipitate absorbs oxygen from the air, and is rapidly converted into ferrous sulphate, and lastly into yellow basic ferric sulphate, with evolution of much heat. (This oxidation constitutes a frequent cause of the spontaneous inflammation of pyritical coal (which contains $\mathbf{Fe}_7O_8$) on board vessels).

$\mathbf{S}H_2$ does not precipitate neutral or acid solutions of ferrous salts; ferrous acetate even is only partially precipitated.

KHo, NaHo, or AmHo precipitates from ferrous salts (free from ferric salts) *white* **ferrous hydrate**, $\mathbf{Fe}Ho_2$, which turns rapidly to a *dirty green* colour, and ultimately becomes *reddish brown*, owing to absorption of oxygen from the atmosphere. Ammonic salts partially prevent the precipitation, and AmHo gives but a slight precipitate in a ferrous solution containing a sufficient amount of AmCl.

$\mathbf{C}ONao_2$, $\mathbf{C}OKo_2$, or $\mathbf{C}OAmo_2$ precipitates *white* **ferrous carbonate**, $\mathbf{C}OFeO''$, which becomes rapidly oxidized when exposed to air.

K_4FeCy_6 (**potassic ferrocyanide**) produces, by the replacement of K_2 by Fe'', a *bluish-white* precipitate of **dipotassic ferrous ferrocyanide**, $K_2Fe''FeCy_6$, thus:—

$$\mathbf{S}O_2Feo'' + K_4FeCy_6 = \underset{\substack{\text{Bluish-white}\\\text{precipitate.}}}{K_2Fe''FeCy_6} + \mathbf{S}O_2Ko_2.$$

insoluble in hydrochloric acid. The light blue precipitate is rapidly converted into a *dark blue* precipitate, or **Prussian blue**, either by exposure to the air, or more speedily by an oxidizing agent, thus:—

$$4K_2Fe''FeCy_6 + 2Cl_2 = \underset{\text{Prussian blue.}}{3FeCy_2,2Fe_2Cy_6} + 4KCl + K_4FeCy_6.$$

$K_6Fe_2Cy_{12}$ (**potassic ferricyanide**) produces a *dark blue* precipitate of **triferrous diferric dodecacyanide**, $Fe''_3\,'Fe'''_2Cy_{12}$ (**Turnbull's blue**), insoluble in hydrochloric acid, thus:—

$$3\mathbf{S}O_2Feo'' + K_6Fe_2Cy_{12} = \underset{\text{Turnbull's blue.}}{Fe''_3\,'Fe'''_2Cy_{12}} + 3\mathbf{S}O_2Ko_2.$$

NaHo or KHo decomposes both precipitates with formation of alkaline ferro- and ferricyanides, and ferrous and ferric hydrates, thus:—

(1) $K_2Fe''FeCy_6 + 2KHo = K_4FeCy_6 + \mathbf{Fe}Ho_2$.
(2) $3FeCy_2,2Fe_2Cy_6 + 12NaHo = 3Na_4FeCy_6 + 2\mathbf{Fe}_2Ho_6$.
(3) $Fe''_3{}'Fe'''_2Cy_{12} + 6NaHo = Na_6Fe_2Cy_{12} + 3\mathbf{Fe}Ho_2$.

These precipitates cannot form, therefore, in an alkaline solution.

CyKs (**potassic sulphocyanate**) gives no indication, if the ferrous contains no ferric salt.

B. Ferric compounds.—We employ A SOLUTION OF FERRIC CHLORIDE, $'\mathbf{Fe}'''_2Cl_6, = \begin{cases} '\mathbf{Fe}'''Cl_3 \\ '\mathbf{Fe}'''Cl_3. \end{cases}$

$\mathbf{S}Am_2$ (**group-reagent**) produces a *black* precipitate of **ferrous sulphide**, $\mathbf{Fe}S$, mixed with S, thus:—$\mathbf{Fe}_2Cl_6 + 3\mathbf{S}Am_2 = 2\mathbf{Fe}S + S + 6AmCl$.

On dissolving the black precipitate in dilute hydrochloric acid, sulphuretted hydrogen is evolved, and white insoluble sulphur is left. (DISTINCTION BETWEEN FERROUS AND FERRIC SALTS.) Sulphur is not capable of forming a ferric sulphide in the wet way; native sulphides exist, however, viz., $\mathbf{Fe}S_2$ and $\mathbf{Fe}_2S_3$, which are insoluble in dilute hydrochloric acid, but dissolve with evolution of $\mathbf{S}H_2$ in the presence of metallic zinc.

$\mathbf{S}H_2$ does not precipitate $\mathbf{Fe}_2Cl_6$; its hydrogen acts as a reducing agent upon the ferric salt, converting it into $2\mathbf{Fe}Cl_2$ and 2HCl; white sulphur being precipitated, which renders the solution of the ferrous salt milky.

KHo, NaHo, or AmHo precipitates the *reddish brown* **ferric hydrate**, $\mathbf{Fe}_2Ho_6$, insoluble in excess and in ammonic salts (except $\mathbf{C}OAmo_2$). Non-volatile organic bodies (*e.g.*, tartaric or citric acid, sugar, etc.,) prevent its precipitation by AmHo, but not by $\mathbf{S}Am_2$. The precipitate retains with great tenacity small portions of the fixed alkalies.

$\mathbf{C}ONao_2$, $\mathbf{C}OKo_2$ and $\mathbf{C}OAmo_2$ produce the same precipitate with evolution of carbonic anhydride.

K_4FeCy_6 gives a *fine blue* precipitate, $3FeCy_2$, $2Fe_2Cy_6$, known as **Prussian blue**, thus:—$2\mathbf{Fe}_2Cl_6 + 3K_4FeCy_6 = 3FeCy_2,2Fe_2Cy_6 + 12KCl$. Insoluble in hydrochloric acid; decomposed by KHo or NaHo; soluble in oxalic acid; soluble also in excess of K_4FeCy_6, to a blue solution.

$K_6Fe_2Cy_{12}$ produces no precipitate, but the yellow colour of the ferric solution changes to *reddish brown*.

CyKs (**potassic sulphocyanate**) gives a *dark red* or *blood red* colour, even in the case of very dilute solutions, which is not destroyed by hydrochloric acid. The sensitiveness of the reaction is heightened by shaking the solution containing mere traces of a ferric salt with ether. The *blood red* **ferric sulphocyanate**, $Cy_6Fe_2s^{vi}$, being soluble in ether, becomes thus concentrated into a small bulk of liquid. The colour of the liquid is readily destroyed by $\mathbf{Hg}\mathrm{Cl_2}$ (also by tartaric or phosphoric acid).

This confirmatory test should invariably be applied, because ferric acetate, when heated in presence of acetic acid, gives likewise a deep red coloration, which becomes lighter coloured on cooling.

Ammonic succinate or **benzoate** precipitates ferric, but not ferrous salts, as **ferric succinate** or **benzoate.*** The ferric solution should be perfectly neutral. Salts of $\mathbf{Fe}\mathrm{O}$, $\mathbf{Mn}\mathrm{O}$, $\mathbf{Co}\mathrm{O}$, $\mathbf{Ni}\mathrm{O}$, $\mathbf{Zn}\mathrm{O}$ are not precipitated. (METHOD OF SEPARATION OF $\mathrm{FE^{iv}}$ FROM MN, NI, CO, ZN.)

Precipitated and well washed **baric** or **calcic carbonate**, suspended in water, precipitates ferric salts (not ferrous salts), as **ferric hydrate**, $\mathbf{Fe}_2\mathrm{Ho_6}$, with evolution of carbonic anhydride. The reagent is added to the ferric salt in the cold and well shaken up with it, till the *reddish brown* precipitate acquires a whitish appearance from excess of the alkaline earthy carbonate.

$\mathbf{C}\mathrm{OBao''}$ separates in like manner the higher chlorides of (Mn, Co) Cr and Al from the lower chlorides. In order to separate ferric from ferrous compounds, or ferric, chromic, and aluminic compounds from ferrous, zincic, manganous, cobaltous, and nickelous salts, it is necessary that these metals should all be obtained in the form of chlorides, when, on the addition of $\mathbf{C}\mathrm{OBao''}$, the respective hydrates are precipitated from the ferric, etc., chlorides, whilst ferrous chloride and the chlorides of Zn, Mn, Ni, and Co, are not affected. Air has to be excluded as carefully as possible; and the reaction should be performed in a small flask, filled nearly to the neck with the liquid, and kept well stoppered, after the evolution of $\mathbf{C}\mathrm{O_2}$ has ceased. (METHOD FOR SEPARATING $\mathrm{Fe^{iv}}$ ($\mathrm{Al^{iv}}$ and $\mathrm{Cr^{iv}}$) FROM FE'', ZN'', MN'', NI'' and CO''.)

The precipitate is filtered off and dissolved in hydrochloric acid; the barium is removed by means of $\mathbf{S}\mathrm{O_2Ho_2}$, and the iron, etc., precipitated by AmHo.

Tannic as well as **gallic acid** (tincture of nut-galls) produces from neutral ferric salts a *bluish black* precipitate (ink), readily soluble in acids.

A very delicate reaction consists in adding a few drops of a solution of potassic ferricyanide to a dilute solution of a ferric salt, and next a few drops of a very dilute solution of stannous chloride, $\mathbf{Sn}\mathrm{Cl_2}$. A blue precipitate indicates the presence of iron, thus :—

(1) $\mathbf{Fe}_2\mathrm{Cl_6} + \mathrm{K_6Fe_2Cy_{12}}$ gives no precipitate, but merely a dark brown coloration.

(2) $\mathbf{Fe}_2\mathrm{Cl_6} + \mathbf{Sn}\mathrm{Cl_2} = 2\mathbf{Fe}\mathrm{Cl_2} + \mathbf{Sn}\mathrm{Cl_4}.$

(3) $3\mathbf{Fe}\mathrm{Cl_2} + \mathrm{K_6Fe_2Cy_{12}} = \mathrm{Fe''_3Fe_2Cy_{12}} + 6\mathrm{KCl}.$
Turnbull's blue.

A ferric salt when coming in contact with certain bodies (especially bodies containing some latent bonds) which possess a stronger affinity for oxygen, chlorine, etc., than the ferric compound, acts towards such bodies as an **oxidizing agent.** Thus $\mathbf{S}^{\mathrm{iv}}\mathrm{OHo_2}$ is converted into $\mathbf{S}^{\mathrm{vi}}\mathrm{O_2Ho_2}$; KI gives off iodine; $\mathbf{Sn}''\mathrm{Cl_2}$ is converted into $\mathbf{Sn}^{\mathrm{iv}}\mathrm{Cl_4}$: $\mathbf{S}\mathrm{SONao_2}$ (sodic hyposulphite) is oxidized to $\mathbf{S}\mathrm{O_2HoNao}$. Iron and zinc readily reduce ferric to ferrous salts.

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* The formulæ of these compounds will be explained under the respective acids.

C. **Ferric anhydride,** $\mathbf{Fe}^{vi}O_3$, or ferric acid, $\mathbf{Fe}^{vi}O_2Ho_2$, containing hexad iron, has never been obtained in an uncombined state. The alkali salts only are known and are obtained, like the alkaline manganates, by fusing iron filings with nitre. Ferrates are decomposed far more readily than manganates.

QUESTIONS AND EXERCISES.

1. Mention compounds illustrative of the dyad, tetrad, and hexad nature of iron.
2. Enumerate some of the most important iron ores used for the extraction of iron in this country. Give constitutional and graphic formulæ.
3. Which are the more important sulphides of iron? Give constitutional and graphic formulæ.
4. Give the graphic formulæ of *chloropal, chrome iron ore, green copperas*, and *vivianite.*
5. How is iron detected in the dry way?
6. What takes place when iron is dissolved in HCl, in $\mathbf{S}O_2Ho_2$, or in dilute $\mathbf{N}O_2Ho$?
7. Explain the change which takes place when $\mathbf{Fe}Cl_2$ is acted upon by atmospheric air, by chlorine, KO_3Cl and HCl, $\mathbf{N}O_2Ho$, $\mathbf{Hg}Cl_2$, $\mathbf{Au}Cl_3$, and by $\mathbf{Mn}_2O_6Ko_2$ and HCl. Express the changes by equations.
8. Give graphic formulæ for ferric chloride, ferric hydrate, ferrous sulphide, dipotassic ferrate.
9. Explain the action of $\mathbf{S}H_2$ and $\mathbf{S}Am_2$ upon ferric salts in acid solutions; 2°, in neutral or alkaline solutions.
10. How does K_4FeCy_6 and $K_6Fe_2Cy_{12}$ enable us to distinguish between ferrous and ferric salts?
11. State why $K_6Fe_2Cy_{12}$, in the presence of $\mathbf{Sn}Cl_2$, produces a blue precipitate with ferric salts.
12. Explain the action of CyKs upon ferrous and ferric salts.
13. Explain the action, 1° of $\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right.$, 2° of KHo, 3° of K_4FeCy_6 upon Prussian blue.
14. What change is produced when $\mathbf{Fe}_2Cl_6$ is brought together, 1°, with $\mathbf{S}O_2$; 2°, with $\mathbf{Sn}Cl_2$?
15. Explain the action of metallic iron or metallic zinc upon $\mathbf{S}_3O_6Fe_2o^{vi}$.
16. How would you prepare dipotassic ferrate? Explain the action, 1°, of water; 2°, of HCl upon it.
17. How much hydrogen gas by weight and volume (at 0° C. and 760 mm.) is obtained when 10 grms. of metallic iron are dissolved in dilute hydrochloric acid?
18. How much sulphurous anhydride gas by weight and by volume is required to reduce 1·324 grm. of ferric sulphate to ferrous sulphate?
19. Calculate the percentage composition of $\mathbf{Fe}S_2$.
20. The value of a ton of Sicilian sulphur (containing 94 per cent. of S) is £5, that of a ton of *iron pyrites*, $\mathbf{Fe}S_2$, containing 46·5 per cent. of sulphur, £1 10*s.* 6*d.* Ascertain which can be more profitably worked in the manufacture of sulphuric acid, having regard merely to the respective sources of sulphur.
21. How much metallic iron is required to manufacture one ton of crystallised *green vitriol?*
22. ·432 grm. of *brown haematite ore* gave ·350 grm. of $\mathbf{Fe}_2O_3$. What is the percentage of metallic iron in the ore, and what the percentage of *brown haematite* present?
23. How is $\mathbf{Fe}_2O_3$ separated from $\mathbf{Fe}O$? Describe two methods.
24. How would you separate $\mathbf{Fe}_2O_3$ from Zn″, Mn″, Ni″, and Co″?
25. Why is it preferred to precipitate $\mathbf{Fe}_2Cl_6$ by means of AmHo, instead of KHo?

CHROMIUM, Cr'', ^{iv} and ^{vi}.—This element is comparatively rare. It occurs in nature chiefly as *chrome iron ore*, $\left\{\begin{matrix}CrO\\CrO\end{matrix}\right.Feo''$, and *crocoisite*, CrO_2Pbo''. Chromic oxide constitutes the colouring matter in ruby, green serpentine, etc.

REACTIONS IN THE DRY WAY.

Chromium compounds are readily recognized by the very characteristic **green** colour which the oxide imparts to *borax* and microcosmic salt, especially in the *reducing* flame. Finely powdered chrome iron ore, when fused in a platinum spoon or crucible with four times its weight of hydric potassic sulphate, and then with the addition of an equal bulk of nitre and $COKo_2$ (equally mixed), yields a *yellow mass* of **potassic chromate**, CrO_2Ko_2, which is soluble in water.

REACTIONS IN THE WET WAY.

Chromic salts can be prepared from the yellow CrO_2Ko_2, or the red dipotassic dichromate, $Cr_2O_5Ko_2$, by heating with dilute hydrochloric acid and adding alcohol, drop by drop, when the yellow solution changes to a deep green solution of $Cr_2Cl_6 = \begin{matrix}'Cr'''Cl_3\\'Cr'''Cl_3\end{matrix}$ in which the Cr exists as a tetrad element.

A lower chloride, $CrCl_2$, has been prepared in which Cr acts as a dyad element; but as it has to be carefully kept from the air to prevent its becoming rapidly oxidized, and as it is of no real practical use, a passing notice of it will suffice.

Chromium is capable of forming three series of compounds*

Chromous compounds containing dyad Cr.	Chromic compounds containing tetrad Cr.	Chromates containing hexad Cr.
$Cr''Cl_2$.	$'Cr'''_2Cl_6$.	$Cr^{vi}O_2Ko_2$.
$Cr''O$.	$'Cr'''_2O_3$.	$Cr^{vi}O_2Pbo''$.
$Cr''Ho_2$.	$'Cr'''_2Ho_6$.	

of which we purpose studying only the two latter.

A. **Chromic Compounds.**—We employ A SOLUTION OF CHROMIC CHLORIDE, Cr_2Cl_6.

SAm_2 **(group-reagent)** precipitates *bluish green* **chromic hydrate**, Cr_2Ho_6, insoluble in excess.

AmHo precipitates the **hydrate**, somewhat soluble in excess, the fluid acquiring a pink tint. The precipitation is complete on boiling.

KHo or NaHo, same precipitate, readily soluble in excess to a green solution; reprecipitated by long-continued boiling or on adding AmCl, whereby the fixed alkali is removed as KCl or NaCl with substitution of AmHo.

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* The intermediate oxides, $\left\{\begin{matrix}CrO\\CrO\end{matrix}\right.Cro''$ (chromous dichromic tetroxide), and CrO_2 (chromic dioxide) cannot be considered here.

$\mathbf{C}ONao_2$ and $\mathbf{C}OAmo_2$ give *greenish* precipitates of **basic carbonates** (varying in composition), somewhat soluble in excess.

$\mathbf{C}OBao''$ precipitates **basic carbonate.** The precipitation takes place in the cold, but is completed only after long digestion.

Chromic compounds may be recognized also by converting the chromic oxide into chromic acid. This may be accomplished:—

1st. By boiling a solution of $\mathbf{Cr}_2Cl_6$ with $\mathbf{Pb}O_2$ and KHo or NaHo. The reaction which takes place, and which is indicated by a change of colour (from *green* to *yellow*), may be expressed thus:—

$$(1)\quad \mathbf{Cr}_2Cl_6 + 6KHo = \underset{\text{Soluble in excess of KHo.}}{\mathbf{Cr}_2Ho_6} + 6KCl.$$

$$(2)\quad \mathbf{Cr}_2Ho_6 + 3\mathbf{Pb}O_2 = \underset{\text{Soluble in KHo.}}{2\mathbf{Cr}O_2Pbo''} + \underset{\text{Soluble in KHo.}}{\mathbf{Pb}O.}$$

On acidulating the solution with acetic acid, a precipitate of plumbic chromate, $\mathbf{Cr}O_2Pbo''$ is obtained.

2nd. By boiling a solution of $\mathbf{Cr}_2Cl_6$ with NaHo and sodic hypochlorite, ClNao, thus:—

$$\mathbf{Cr}_2Ho_6 + 3ClNao + 4NaHo = \underset{\text{Yellow disodic chromate.}}{2\mathbf{Cr}O_2Nao_2} + 3NaCl + 5\mathbf{O}H_2.$$

B. **Chromic anhydride,** $\mathbf{Cr}^{vi}O_3$.—Chromic acid, $\mathbf{Cr}O_2Ho_2$, combines with KHo to form two salts, the *normal*, or *yellow chromate*, $\mathbf{Cr}O_2Ko_2$, and the orange *red dichromate*, $\left\{\begin{array}{l}\mathbf{Cr}O_2Ko\\ O\\ \mathbf{Cr}O_2Ko\end{array}\right.$, isomorphous with the corresponding sulphate and disulphate.

The anhydride may be prepared by slowly adding to a cold saturated solution of the red dipotassic dichromate 1½ times its bulk of concentrated sulphuric acid, and allowing it to cool slowly. $\mathbf{Cr}O_3$ crystallises out in brilliant crimson red prisms. The mother-liquor is poured off, and the crystals placed to drain upon a porous tile or slab of unglazed porcelain (biscuit) and kept covered with a bell-jar. They must be preserved in a well-stoppered bottle.

Chromic anhydride is one of the most powerful oxidizing agents known; two molecules of $\mathbf{Cr}O_3$ can yield three atoms of oxygen, according to the equation:—

$$\mathbf{Cr}O_3 = \mathbf{Cr}_2O_3 + O_3.$$

The metal chromium appears to exist in nature mostly in the tetrad and hexad state, as a glance at its natural compounds will show. Chromium differs, however, in a marked manner from iron and manganese, which can likewise exist in the tetrad and hexad state, by forming more stable hexad compounds (chromates), whilst in perchromic acid, on the other hand, the metal chromium appears to hold the oxygen less firmly than manganese holds it in permanganic acid.

REACTIONS FOR $\mathbf{Cr}O_3$ BASED UPON ITS OXIDIZING ACTION.

A SOLUTION OF DIPOTASSIC DICHROMATE, $\mathbf{Cr}_2O_5Ko_2$, may be employed.

$\mathbf{S}H_2$, in the presence of free hydrochloric acid, reduces the orange red solution to a green liquid, sulphur only being precipitated, thus:—

$$\mathbf{Cr}_2O_5Ko_2 + 8HCl + 3\mathbf{S}H_2 = \mathbf{Cr}_2Cl_6 + 2KCl + 7\mathbf{O}H_2 + S_3.$$

$\mathbf{S}Am_2$, added in excess to a solution of an alkaline chromate or dichromate, precipitates *dirty green* **hydrated chromic chromate.** On boiling, the whole of the chromium separates as *green* **chromic hydrate**, thus:—

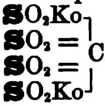
$$\mathbf{Cr}_2O_5Ko_2 + 3\mathbf{S}Am_2 + 7\mathbf{O}H_2 = \mathbf{Cr}_2Ho_6 + S_3 + 2KHo + 6AmHo.$$

In the one case the H_2 of the $\mathbf{S}H_2$ acted as the reducing agent; in the other the $(NH_4)_2$ of the $\mathbf{S}Am_2$.

$\mathbf{S}OHo_2$, in the presence of a little free $\mathbf{S}O_2Ho_2$, reduces the dichromate to chromic sulphate, thus:—

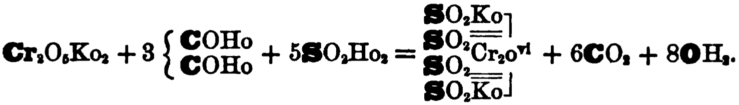
$$\mathbf{Cr}_2O_5Ko_2 + 3\mathbf{S}OHo_2 + 2\mathbf{S}O_2Ho_2 = \mathbf{S}_3O_6Cr_2o^{vi} + \mathbf{S}O_2Ko_2 + 5\mathbf{O}H_2.$$

Chromic sulphate and potassic sulphate constitute potassium chrome alum, or (dipotassic chromic tetrasulphate)



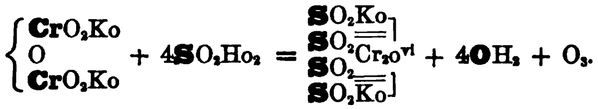
$$\left.\begin{array}{l}\mathbf{S}O_2Ko-\\ \mathbf{S}O_2=\\ \mathbf{S}O_2=\\ \mathbf{S}O_2Ko-\end{array}\right]Cr_2o^{vi}.$$

$\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}OHo\end{array}\right.$ **(oxalic acid)**, in the presence of free acid (dilute sulphuric acid), produces the same reaction, carbonic anhydride being evolved. Six molecules of $\mathbf{C}O_2$ become the measure for one molecule of dipotassic dichromate. Tartaric and citric acid act in like manner.



$$\mathbf{Cr}_2O_5Ko_2 + 3\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}OHo\end{array}\right. + 5\mathbf{S}O_2Ho_2 = \left.\begin{array}{l}\mathbf{S}O_2Ko-\\ \mathbf{S}O_2=\\ \mathbf{S}O_2=\\ \mathbf{S}O_2Ko-\end{array}\right]Cr_2o^{vi} + 6\mathbf{C}O_2 + 8\mathbf{O}H_2.$$

$\mathbf{S}O_2Ho_2$ (concentrated) reduces the dichromate, on the application of heat, with evolution of oxygen and formation of potassium chrome alum, thus:—



$$\left\{\begin{array}{l}\mathbf{Cr}O_2Ko\\ O\\ \mathbf{Cr}O_2Ko\end{array}\right. + 4\mathbf{S}O_2Ho_2 = \left.\begin{array}{l}\mathbf{S}O_2Ko-\\ \mathbf{S}O_2=\\ \mathbf{S}O_2=\\ \mathbf{S}O_2Ko-\end{array}\right]Cr_2o^{vi} + 4\mathbf{O}H_2 + O_3.$$

HCl (concentrated) evolves chlorine, and the hydrogen combines with the three available atoms of oxygen in the dichromate, thus:—

$$\left\{\begin{array}{l}\mathbf{Cr}O_2Ko\\ O\\ \mathbf{Cr}O_2Ko\end{array}\right. + 14HCl = \mathbf{Cr}_2Cl_6 + 2KCl + 7\mathbf{O}H_2 + 3Cl_2.$$

$\mathbf{As}_2O_3$ (in a hydrochloric acid solution) is converted into $\mathbf{As}OHo_3$, thus:—

$$\left\{\begin{array}{l}\mathbf{Cr}O_2Ko\\ O\\ \mathbf{Cr}O_2Ko\end{array}\right. + 3\mathbf{As}Ho_3 + 8HCl = \mathbf{Cr}_2Cl_6 + 2KCl + 3\mathbf{As}OHo_3 + 4\mathbf{O}H_2.$$

$\mathbf{Sn}Cl_2$, $\mathbf{Sb}Cl_3$, $\mathbf{Fe}Cl_2$, Zn (Fe, Sn, etc.) in the presence of dilute HCl reduce likewise chromates or dichromates.

REACTIONS FOR $\mathbf{Cr}O_3$ PRODUCED BY DOUBLE DECOMPOSITION.

Chromates of the alkalies and alkaline earthy bases (with the exception of baric chromate, $\mathbf{Cr}O_2Bao''$,) also of manganese and copper, are soluble in water; all other chromates are insoluble, but dissolve readily in dilute nitric acid.

$\mathbf{Ba}Cl_2$, added to a solution of a normal chromate or dichromate, gives a *light lemon yellow* precipitate of **baric chromate**, $\mathbf{Cr}O_2Bao''$, even in very dilute solutions; insoluble in acetic acid, readily soluble in nitric or hydrochloric acid, and reprecipitated by AmHo.

$\begin{array}{l}\left\{\begin{array}{l}CH_3\\ CO\end{array}\right.\\ \left\{\begin{array}{l}CO\\ CH_3\end{array}\right.\end{array} Pbo''$ (**plumbic acetate**) gives a *fine lemon yellow* precipitate of **plumbic chromate**, $\mathbf{Cr}O_2Pbo''$, soluble in KHo, sparingly soluble in dilute nitric, insoluble in acetic acid.

$\mathbf{N}O_2Ago$ (**argentic nitrate**) gives a *dark purple red* precipitate of **diargentic chromate**, $\mathbf{Cr}O_2Ago_2$, soluble in nitric acid and ammonia. From weak acid solutions **diargentic dichromate**, $\left\{\begin{array}{l}\mathbf{Cr}O_2Ago\\ O\\ \mathbf{Cr}O_2Ago\end{array}\right.$, is precipitated.

$\begin{array}{l}\mathbf{N}O_2\\ \mathbf{N}O_2\end{array}Hg_2o''$ (**mercurous nitrate**) gives a *dark brick red* basic precipitate of $\mathbf{Cr}OHg_2o''Hg_2o''$, which on ignition is converted into oxygen, mercury, and fine green $\mathbf{Cr}_2O_3$. (METHOD OF SEPARATING CHROMIC ACID FROM CHROMIC OXIDE.)

On bringing together a little chromic acid with hydric peroxide, $\mathbf{O}_2H_2$, in an aqueous solution, a deep indigo-blue solution is produced, owing probably to the formation of PERCHROMIC ACID, in which chromium plays the part of a pseudo-octad element, analogous to permanganic acid.

A solution of perchromic acid decomposes, however, rapidly with evolution of oxygen, leaving $\mathbf{Cr}O_2Ho_2$; and its constitution is yet doubtful. A solution in ether is far more stable than an aqueous solution. It is obtained by adding ether to a very dilute solution of $\mathbf{O}_2H_2$ and then a drop of a dilute solution of a chromate. On shaking up gently the ether takes up the whole of the perchromic acid, and acquires an intense blue colour. Mere traces of $\mathbf{Cr}O_3$ can be discovered in this manner, or *vice versâ* the smallest quantities of $\mathbf{O}_2H_2$.

QUESTIONS AND EXERCISES.

1. Which is the most important chromium ore? Give symbolic and graphic formula.

2. How is chromium detected in the dry way?
3. What analogy exists there between *chrome iron ore* and chromous dichromic tetroxide?
4. Describe how chromic chloride or sulphate is obtained from an alkaline chromate.
5. Give symbolic and graphic formulæ for dipotassic chromate and dichromate, and trace their analogy with the corresponding sulphates.
6. Describe the reactions by double decomposition which you can produce with chromic compounds. Give equations.
7. How can chromic compounds be converted in the wet way into chromates? Give instances and express the changes by equations.
8. How is chromic anhydride prepared?
9. Give instances of the oxidizing action of chromic acid. Express the changes by symbolic equations.
10. What is the composition of potassium chrome alum? State shortly by what processes it is prepared from *chrome iron ore*.
11. You have given to you oxalic, hydrochloric and concentrated sulphuric acids, dipotassic dichromate and water. State how you would prepare $\mathbf{C}O_2$, O, or Cl gas from these materials, and express the changes by equations.
12. What is the action of nascent hydrogen upon alkaline chromates? Give several instances and express the changes by equations.
13. Describe some of the most characteristic reactions for chromic acid produced by double decomposition. Give equations.
14. How would you distinguish between chromic oxide and chromic acid occurring in one and the same solution?
15. Which chromates are soluble and which are insoluble in water?
16. What evidence is there for the existence of perchromic acid?
17. How can we test for mere traces of hydric peroxide?
18. Calculate the percentage composition of potassium chrome alum, containing 24 molecules of water of crystallisation.
19. How can Cr be separated from every other metal of Group III, except **Mn**?
20. How can $\mathbf{Cr}_2O_3$ be separated from Fe'', Zn'', $\mathbf{Mn}''$, Ni'', Co'' salts?
21. 1·600 grm. of *chrome iron ore* yielded 2·95 grms. of $\mathbf{Cr}O_2Pbo''$. What percentage of Cr does the ore contain, and how much dipotassic dichromate can be manufactured from one ton of the ore?
22. 1·2 grm. of a sample of sodic chromate yielded with $\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right.$ ·89 grm. of $\mathbf{C}O_2$. What percentage of chromic anhydride did it contain?

ALUMINIUM, Al'' and ^{iv}.—One of the metallic elements which occurs most abundantly in nature, both in the form of the OXIDE and as an important constituent of many minerals, in combination with SILICA, with SULPHURIC, PHOSPHORIC, and other acids; and in the form of FLUORIDE in *cryolite*, and the rare *topaz*. For a list of some of the more interesting aluminic compounds the student is referred to "Lecture Notes," page 179.

REACTIONS IN THE DRY WAY.

Alumina, when heated on charcoal, is distinguished from other earths by its property of assuming a beautiful blue colour, after being moistened with a solution of cobaltous nitrate and ignited once more strongly. This test becomes inapplicable when coloured oxides, such as $\mathbf{Fe}_2O_3$, $\mathbf{Mn}O$, etc., are present, in which case recourse must be had to the examination in the wet way, in order to discover $\mathbf{Al}_2\mathrm{O}_3$.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF AMMONIUM ALUM, $\mathbf{S}_4\mathrm{O}_8\mathrm{Amo}_2\mathrm{Al}_2\mathrm{o}^{\mathrm{vi}}$, in which Al plays the part of a tetrad (pseudo-triad) element, or of *aluminic chloride*, $\left\{\begin{matrix} '\mathbf{Al}'''\mathrm{Cl}_3 \\ '\mathbf{Al}'''\mathrm{Cl}_3 \end{matrix}\right.$.

$\mathbf{S}\mathrm{Am}_2$ gives a *white gelatinous* precipitate of **aluminic hydrate**, $\mathbf{Al}_2\mathrm{Ho}_6$, sulphuretted hydrogen being evolved, thus :—

$$\mathbf{S}_4\mathrm{O}_8\mathrm{Amo}_2\mathrm{Al}_2\mathrm{o}^{\mathrm{vi}} + 3\mathbf{S}\mathrm{Am}_2 + 6\mathbf{O}\mathrm{H}_2 = \mathbf{Al}_2\mathrm{Ho}_6 + 4\mathbf{S}\mathrm{O}_2\mathrm{Amo}_2 + 3\mathbf{S}\mathrm{H}_2.$$

KHo or NaHo* precipitates the **hydrate**, readily soluble in excess, reprecipitated by excess of AmCl, or by AmHo, after neutralization of the alkali by hydrochloric acid. The alkaline solution is not precipitated by $\mathbf{S}\mathrm{Am}_2$.

AmHo precipitates the **hydrate**, somewhat soluble in excess, insoluble in the presence of much ammonic chloride, and on boiling.

$\mathbf{C}\mathrm{ONao}_2$ or $\mathbf{C}\mathrm{OAmo}_2$ precipitates **basic carbonate** of uncertain composition.

$\mathbf{C}\mathrm{OBao}''$ precipitates $\mathbf{Al}_2\mathrm{Ho}_6$ mixed with **basic salt**, very slowly in the cold.

$\mathbf{P}\mathrm{OHoNao}_2$ gives a *bulky white* precipitate of **aluminic phosphate**, $\mathbf{P}_2\mathrm{O}_2\mathrm{Al}_2\mathrm{o}^{\mathrm{vi}}$, insoluble in AmHo and AmCl; soluble in NaHo, like the hydrate (AmCl reprecipitates the phosphate from the soda solution), and in acids, but not in hot acetic acid (DISTINCTION OF $\mathbf{Al}_2\mathrm{O}_3$ FROM ALUMINIC PHOSPHATE). Alkaline acetates precipitate $\mathbf{P}_2\mathrm{O}_2\mathrm{Al}_2\mathrm{o}^{\mathrm{vi}}$ from its solution in mineral acids.

In order to decompose aluminic phosphate (*e.g.*, in the mineral *wavellite*, $\mathbf{P}_4\mathrm{O}(\mathrm{Al}_2\mathrm{o}^{\mathrm{vi}})_3,12\mathbf{O}\mathrm{H}_2$), it is best to fuse the finely powdered mineral with 1¼ part of finely divided $\mathbf{Si}\mathrm{O}_2$ and 6 parts of $\mathbf{C}\mathrm{ONao}_2$, in a platinum crucible, for about half an hour. The mass is digested for some time with water, and $\mathbf{C}\mathrm{OHoAmo}$ added in excess; it is then filtered and washed. The residue consists of aluminic and sodic silicate, the solution contains the sodic phosphate. Dissolve the residue in dilute hydrochloric acid, and evaporate to dryness to separate $\mathbf{Si}\mathrm{O}_2$, and filter. The filtrate may be tested for Al in the usual way.

Alumina occurs mostly in minerals which are not soluble in acids. Boiling with concentrated sulphuric acid attacks many; all are, however, decomposed by fusion with $\mathbf{S}\mathrm{O}_2\mathrm{HoKo}$, or with fusion mixture, and become readily soluble in water, or in dilute hydrochloric acid (compare Chapter XIX).

Powder up some porcelain very finely, and fuse for half an hour in a platinum crucible with four times its weight of fusion mixture. Extract with water. Transfer to a porcelain dish, acidulate with hydrochloric acid, and evaporate to dryness. Take up with a few drops of concentrated hydrochloric acid and hot water, and filter; wash the insoluble $\mathbf{Si}O_2$ well with hot water. The filtrate contains the aluminium as $\mathbf{Al}_2Cl_6$, from which it can be precipitated as usual.

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* Potassic or sodic hydrate is mostly contaminated with alumina, derived during the manufacture from porcelain vessels, etc., and it is, therefore, absolutely necessary to employ pure NaHo (prepared from sodium) for the separation of Fe and Al. It must likewise be recollected that NaHo acts destructively upon porcelain and glass vessels; the precipitate should, therefore, not be heated longer than is necessary for its complete precipitation.

Aluminic silicate is often found in nature associated with potassic or sodic silicate, as in *felspar* (dipotassic aluminic hexasilicate), $\mathbf{Si}_6O_8Ko_2Al_2o^{vi}$, and *albite*, $\mathbf{Si}_6O_8Nao_2Al_2o^{vi}$. In order to test for potassium and sodium, alkali salts must, of course, be carefully avoided. This can be done by making use of hydrofluoric acid.

Introduce a small quantity of finely powdered *felspar* into a platinum crucible or dish; treat with liquid hydrofluoric acid, and evaporate at a gentle heat in a cupboard which is connected with the chimney. HF attacks the $\mathbf{Si}O_2$, forming silicic fluoride, $\mathbf{Si}F_4$—a volatile compound—and leaves the aluminium and potassium behind as fluorides readily soluble in dilute hydrochloric acid:—

$$\mathbf{Si}_6O_8Ko_2Al_2o^{vi} + 32HF = 6\,\mathbf{Si}F_4 + 2KF + \mathbf{Al}_2F_6 + 16\mathbf{O}H_2.$$

The decomposition is generally only completed after two or three evaporations with HF.

QUESTIONS AND EXERCISES.

1. Enumerate some of the more important aluminium minerals; give constitutional and graphic formulæ.
2. How is $\mathbf{Al}_2O_3$ detected in the dry way?
3. Give equations for the reactions of aluminium in the wet way.
4. How is *wavellite* examined for alumina?
5. How is *felspar* examined for alumina?
6. How can insoluble aluminium minerals be rendered soluble in water or acids?
7. Explain the action of HF upon *felspar* and *albite*.
8. How can $\mathbf{Al}_2O_3$ be separated from $\mathbf{Fe}_2O_3$?
9. How is $\mathbf{Al}_2O_3$ separated from Fe″, Zn″, Mn″, Ni″, Co″ compounds?
10. Calculate the percentage composition of *felspar*.
11. What changes take place when ammonium alum is strongly ignited?
12. How can $\mathbf{Al}_2O_3$ be distinguished from $\mathbf{P}_2O_2Al_2o^{vi}$?

The separation of the metals of Group III is surrounded by some difficulties, on account of the unavoidable complication which arises from the possibly simultaneous precipitation of—

1st *Sulphides*, viz., **Ni**S, **Co**S, **Mn**S, **Zn**S, **Fe**S.
2nd. *Hydrates*, viz., $\mathbf{Cr}_2Ho_6$, $\mathbf{Al}_2Ho_6$, and
3rd. *Phosphates* of Cr, Al, Ba, Sr, Ca, Mg,

and it is therefore well always to ascertain, by a special experiment, whether phosphoric acid, in combination with the above metals, is present or not in the solution under examination.

This can readily be done by adding AmCl, AmHo, and $\mathbf{S}Am_2$ to a small portion of the solution (or to the filtrate from Group II). On dissolving the precipitate which these reagents produce in dilute hydrochloric acid, with the addition of a few crystals of KO_3Cl, and adding a solution of ammonic molybdate,* a yellow precipitate is obtained (especially on digesting for some time at a gentle heat), showing the presence of phosphoric acid. If no precipitate is obtained, the solution need only be examined for Ni, Co, Mn, Zn, Fe, Al, and Cr.

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* For the preparation of this reagent see Appendix.

I. **Phosphoric acid is absent.**—This is sufficiently indicated, if the original substance dissolved readily in water. If insoluble in water, but soluble in dilute acids, phosphoric acid may likewise be absent from the substance, but not necessarily so.

It would appear at first sight that the deportment of the five sulphides and two hydrates with ammonic chloride and ammonic hydrate, sodic or potassic hydrate, or dilute acids (*ex. gr.*, HCl), would enable us to separate the members of this group, or several of them, from each other. We have seen for example that—

1st. *Ni, Co, Mn, Zn are not precipitated by AmHo from a solution containing large excess of AmCl; whilst* $\mathbf{Fe}_2Ho_6$, $\mathbf{Cr}_2Ho_6$, *and* $\mathbf{Al}_2Ho_6$ *are precipitated.* It has, however, been found that the mode of separation, based upon this solvent property of ammonic chloride, gives very imperfect results; since the $\mathbf{Fe}_2Ho_6$ carries down varying quantities of the other oxides, especially on exposure of the solution to the air, when higher oxides of manganese, etc., are formed which are not soluble in ammonic chloride. Small quantities of Ni, Co, Mn, and Zn are thus frequently overlooked altogether. It is only by redissolving the precipitate and reprecipitating several times over with AmCl and AmHo, till the filtrate gives no longer a precipitate with $\mathbf{S}Am_2$, that iron can be separated from manganese, etc., in this manner.

2nd. *That Zn, Al and Cr are precipitated by KHo or NaHo, but are soluble in excess; whilst the other metallic hydrates are insoluble.* From this it would appear that these three metals can be separated by means of the fixed alkaline hydrates. But it has been found that $\mathbf{Fe}_2Ho_6$, $\mathbf{Ni}Ho_2$, $\mathbf{Co}Ho_2$, $\mathbf{Mn}Ho_2$ carry down appreciable quantities of $\mathbf{Zn}Ho_2$ and—more especially the $\mathbf{Fe}_2Ho_6$ precipitate—of $\mathbf{Cr}_2Ho_6$, and that a complete separation cannot be effected by precipitation with KHo or NaHo.

3rd. *Cold dilute hydrochloric acid does not dissolve* $\mathbf{Co}S$ *or* $\mathbf{Ni}S$ *to any great extent, but dissolves the other sulphides and hydrates.* This method, if practised with care, gives good results; small traces only of $\mathbf{Co}S$ and $\mathbf{Ni}S$ being generally dissolved out. But as it leaves the iron, aluminium and chromium still to be separated from manganese and zinc, no saving of labour is effected thereby in the separation of these seven metals.

In finely divided, freshly precipitated **baric carbonate,** $\mathbf{C}OBao''$, *we possess a reagent which separates the lower oxides, viz.,* $\mathbf{Zn}O$, $\mathbf{Mn}O$, $\mathbf{Ni}O$, $\mathbf{Co}O$ (this latter not quite so perfectly), *from the higher oxides, viz.,* $\mathbf{Fe}_2O_3$, $\mathbf{Al}_2O_3$, and $\mathbf{Cr}_2O_3$. The metals should be first obtained as chlorides.

The examination of the *precipitate* produced by $\mathbf{C}OBao''$ is based upon—

1st. The *solubility of* $\mathbf{Al}_2Ho_6$ *in NaHo.*

2nd. The *conversion* of $\mathbf{Cr}_2O_3$ *into* $\mathbf{Cr}O_3$ *by fusion with sodic carbonate and nitre, or by boiling with ClNao,* or with $\mathbf{Pb}O_2$ *in an alkaline solution.*

The examination of the *filtrate* is based upon—

1st. The *solubility* of $\mathbf{Zn}Ho_2$ *in sodic hydrate.*

2nd. „ „ $\mathbf{Mn}S$ *in acetic acid.*

3rd. The *formation of soluble* $K_6Co_2Cy_{12}$ *and the precipitation of* Ni *as black* $\mathbf{Ni}_2Ho_6$ *by* ClNao *or chlorine.*

Directions for the separation of these seven metals will be found in the analytical tables under Group IIIA.

PRACTICAL EXERCISES* ON GROUPS IIIA, IV and V.

You are requested to analyze—

1. A solution of ferric chloride, ammonium alum and manganous chloride, containing ·500 grm. of Fe, ·050 grm. of Mn, and ·050 grm. of Al.
2. A solution of $\mathbf{S}O_2Nio''$ and $\mathbf{N}_2O_4Coo''$, containing ·050 grm. of Ni and ·010 grm. of Co.
3. A mixture of the solid salts: zinc white, green vitriol and potassium alum; both in the dry and in the wet way.
4. A solution of $\mathbf{S}O_2Zno''$ and potassium chrome alum, containing ·500 grm. of Cr and ·050 of Zn.
5. A mixture of potassium chrome alum and green vitriol (about ·050 grm.), in the dry way only.
6. A mixture consisting of ferric oxide, manganic oxide and zincic oxide containing ·050 grm. of $\mathbf{Fe}_2O_3$, ·010 grm. of $\mathbf{Mn}O_2$ and ·100 grm. of $\mathbf{Zn}O$; to be examined in the dry way only.
7. A sample of *dolomite*, for Fe'' (Mn) Ca and Mg.
8. A sample of *calc spar*, for Fe'' and Mg.
9. Samples of iron ores, *e.g.*, *red hæmatite*, *brown hæmatite*, *magnetic iron ore*, *martial pyrites*, to be examined for water and sulphur only.
10. A sample of *calamine*, in the dry way only.
11. A sample of *chrome iron ore* for chromium in the dry way only.
12. A sample of *magnetic iron ore* for Fe'', in the wet way.

Tabulate the reactions produced by AmCl and AmHo, NaHo or $\mathbf{S}Am_2$ with the members of Group IIIA, according to the following scheme—

Reagent.	$\mathbf{Al}_2O_3$.	$\mathbf{Cr}_2O_3$.	$\mathbf{Fe}_2O_3$.	$\mathbf{Zn}O$.	$\mathbf{Mn}O$.	$\mathbf{Ni}O$.	$\mathbf{Co}O$
AmCl, and AmHo.	A *white gelatinous* precipitate of $\mathbf{Al}_2Ho_6$, slightly soluble in excess, reprecipitated on boiling.						
NaHo.	Ditto, soluble in excess.						
$\mathbf{S}Am_2$.	A white gelatinous precipitate of $\mathbf{Al}_2Ho_6$, insoluble in excess.						

with the main view of fixing upon the memory the solubility or insolubility of the precipitates in excess of the reagents.

II. **Phosphoric Acid is present.**—The original substance was either insoluble or only partially soluble in water, but soluble in hydrochloric acid. In this case AmCl and AmHo† produce a precipitate, before $\mathbf{S}Am_2$ is added; the precipitate may possibly consist of $\mathbf{Ni}S$, $\mathbf{Co}S$, $\mathbf{Mn}S$, $\mathbf{Zn}S$, $\mathbf{Fe}S$, $\mathbf{Al}_2Ho_6$, $\mathbf{Cr}_2Ho_6$, as well as the phosphates of (Cr), Al, Mg, Ca, Sr, Ba.

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* These exercises may of course be varied, and should be looked upon merely as indicative of the course to be pursued.

† If AmCl and AmHo should give no precipitate, it is obvious that no phosphates and no Fe, Al and Cr need be looked for.

It is obvious that ammonic phosphate is formed by the decomposition of the phosphates of the metals Ni, Co, Mn, Zn, Fe (if present) by $\mathbf{S}Am_2$—AmCl and AmHo precipitate these phosphates without decomposition—which, in its turn, would act upon any soluble salts of Mg, Ba, Sr, Ca, and precipitate phosphates of these metals, although none may have been present originally in the saline mixture. An example will make this clear. Let us suppose that the substance under examination consists of $\mathbf{C}OBao''$, $\mathbf{P}_2O_2Cao''_3$ and $\mathbf{P}_2O_2Fe_2o^{vi}$. On dissolving in hydrochloric acid, baric chloride is formed, and the calcic and ferric phosphates are dissolved without decomposition. On adding AmCl and AmHo, a yellowish white precipitate of $\mathbf{P}_2O_2Fe_2o^{vi}$ and $\mathbf{P}_2O_2Cao''_3$ is obtained, whilst $\mathbf{Ba}Cl_2$ is not precipitated. On adding, however, the AmCl and AmHo, as well as the $\mathbf{S}Am_2$, to the solution, $\mathbf{P}_2O_2Fe_2o^{vi}$ is decomposed into $\mathbf{Fe}S$ and $\mathbf{P}OAmo_3$, which latter, by acting upon the $\mathbf{Ba}Cl_2$, would precipitate baric phosphate. In order to avoid this, the precipitate produced in Group III by AmCl and AmHo, which contains for the most part the whole of the phosphates, is filtered off, and $\mathbf{S}Am_2$ added to the filtrate only. The two precipitates are washed separately, transferred to a porcelain dish and boiled with a little $\mathbf{S}Am_2$, which decomposes the metallic phosphates (possibly also some $\mathbf{Fe}_2Ho_6$); leaving the phosphates of the earths and alkaline earthy bases (if any), as well as the hydrates of Cr and Al, unchanged. The insoluble residue is filtered off and washed with hot water (to which a little $\mathbf{S}Am_2$ has been added to prevent oxidation of $\mathbf{Fe}S$, etc.); the filtrate is tested for phosphoric acid by means of AmCl, AmHo and $\mathbf{S}O_2Mgo''$. A white crystalline precipitate shows that phosphoric acid was present, *in combination with the metals precipitable as sulphides.*

The residue is dissolved in a little hot hydrochloric acid (with the addition of a few crystals of potassic chlorate, if necessary). Add some ammonic molybdate to a portion of the hydrochloric solution and heat gently. In the absence of a yellow precipitate, no phosphates of (Cr), Al, Ba, Sr, Ca, Mg need be looked for; and the solution may be examined according to Table IIIA; whilst a yellow precipitate indicates *that phosphates of the earths or alkaline earthy bases* are present, in addition to the metallic phosphates.

Add an excess of a solution* containing sodic acetate and strong acetic acid: $\mathbf{P}_2O_2Fe_2o^{vi}$, (as well as $\mathbf{P}_2O_2Cr_2o^{vi}$ and $\mathbf{P}_2O_2Al_2o^{vi}$, if present), are precipitated. Any phosphates of the alkaline earths left undecomposed by the ferric chloride, are held in solution by the acetic acid. To the filtrate add $\mathbf{Fe}_2Cl_6$, drop by drop, as long as a precipitate† is obtained, and till the colour of the supernatant liquid becomes distinctly reddish. Digest at a gentle heat; allow to subside and filter. In this manner the whole of the phosphates of the alkaline earthy bases are decomposed, with formation of $\mathbf{P}_2O_2Fe_2o^{vi}$, insoluble in acetic acid—(which precipitate may be neglected), and chlorides of Mg, Ba, Sr, Ca which remain in solution, together with the chlorides of Ni, Co, Mn, Zn (and the excess of $\mathbf{Fe}_2Cl_6$ added). The precipitate produced by AmCl, AmHo and $\mathbf{S}Am_2$, from which the whole of the phosphoric acid has been thus removed, can be examined according to Table IIIA. The alkaline earthy metals are separated according to Tables IV and V. It should be borne in mind that these metals can have been present in the original substance only as phosphates, and the filtrate containing these metals should on no account be mixed up with the main filtrate from Group III, but should be examined separately.

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* For the preparation of this solution see Appendix.

† Phosphates of the alkaline earthy bases must be absent, if $\mathbf{Fe}_2Cl_6$ produces no precipitate *with a portion of the acetic acid solution*, and no ferric salt need then be added to the filtrate. (The presence of iron, other than phosphate, is generally indicated by the reddish colour of the filtrate.) In this case Al and Cr will likewise have to be looked for in the filtrate.

It may be of interest, occasionally, to ascertain, whether any oxalates of Ba, Sr, Ca, and Mg (which are destroyed by evaporation with nitric acid and ignition, before proceeding to Group III), were present in the original mixture, in which case the evaporation to dryness and ignition must be omitted.

The precipitate produced in Group III by AmCl and AmHo alone contains the oxalates, as well as the phosphates of the alkaline earthy bases, and possibly also silica. The oxalates are decomposed by gently igniting the precipitate. The ignited mass is extracted with dilute hydrochloric. Silica, if present, is rendered insoluble and may be separated by filtration. To the acid solution, which may possibly contain phosphates of Mg, Ca, Sr and Ba, as well as chlorides of the bases, present before ignition as oxalates, add AmCl and AmHo and filter off. The filtrate contains the chlorides of Ba, Sr, Ca, and Mg, and is tested separately according to Tables IV and V. ALL BASES SO DISCOVERED MUST HAVE BEEN PRESENT ORIGINALLY AS OXALATES.

We may, then, sum up by stating that THE SEPARATION OF THE METALS AND SALTS (PHOSPHATES) PRECIPITATED IN GROUP IIIB is based upon:—

1st. *The insolubility of the phosphates of Fe, Al, and Cr in acetic acid, in the presence of alkaline acetates.*

2nd. *The separation of the whole of the phosphoric acid which is in combination with the alkaline earthy bases, by means of* $\mathbf{Fe}_2Cl_6$, *in an acetic solution.*

All other operations are identical with those described in Tables IIIA, IV, and V.

A tabular scheme for their examination* will be found in the analytical tables, under Group IIIB.

QUESTIONS AND PRACTICAL EXERCISES ON GROUP IIIB.

You are requested to analyze:—

1. A hydrochloric acid solution, containing common sodic phosphate, ferric chloride, calcic and magnesic chlorides.
2. A hydrochloric acid solution, containing common sodic phosphate, nickelous sulphate, cobaltous nitrate, zincic sulphate, and ferric chloride.

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* The examination of Group IIIB, containing phosphates, may be deferred until the student has become acquainted with the reactions for acids.

3. A hydrochloric acid solution of calcic phosphate, chromic chloride, and aluminic phosphate.
4. A mixture of bone-ash and much ferric oxide.
5. A mixture containing little ferric oxide and much *magnesite* (or *magnesia alba*) and *bone-ash*.
6. A hydrochloric acid solution of common alum and hydric disodic phosphate.
7. How would you recognize alumina in the presence of aluminic phosphate?
8. Given a reddish coloured solution (owing to the presence of ferric salts), which gives a copious precipitate on the addition of sodic acetate and acetic acid in the cold, leaving the solution still coloured. What inference is to be drawn from this observation?
9. A solution contains chromic chloride, chromic phosphate, and dipotassic dichromate. State how you would distinguish these three chromium compounds from each other.
10. An acid solution (HCl) of a mixture, consisting of ferric chloride, baric chloride, and common sodic phosphate, retains its reddish colour, after precipitation with sodic acetate and acetic acid. What inference must be drawn from this, and what would you infer, if the filtrate were colourless, but gave no further precipitate on the addition of $\mathbf{Fe}_2Cl_6$?
11. You have a solution given to you which gives a precipitate with AmCl and AmHo. What inference must you draw, if the filtrate gives no further precipitate on the addition of $\mathbf{S}Am_2$?
12. You have given to you a concentrated solution of ferric chloride. On adding a few drops of a solution of hydric disodic phosphate, a yellowish precipitate appears. Explain what takes place, 1st. When a portion of the solution in which the precipitate is suspended is boiled. 2nd. When acetic acid is added, in the cold, to another portion. 3rd. When the precipitate is filtered and treated with excess of the hydric disodic phosphate, in the presence of ammonia.

CHAPTER V.

REACTIONS OF THE METALS OF GROUP II.

THIS group comprises the metals MERCURY, LEAD, BISMUTH, COPPER, CADMIUM, ARSENIC, ANTIMONY, TIN (GOLD and PLATINUM), which are precipitated from acid solutions (HCl) by means of sulphuretted hydrogen.

Mix together solutions of $\mathbf{N}_3O_6Bio'''$, $\mathbf{Hg}Cl_2$, $\mathbf{S}O_2Cuo''$, $\mathbf{Cd}Cl_2$, $\mathbf{As}_2O_3$ (dissolved in HCl), $\mathbf{N}_2O_4Pbo''$, $\mathbf{Sb}Cl_3$, $\mathbf{Sn}Cl_2$, and $\mathbf{Sn}Cl_4$, and pass a current of $\mathbf{S}H_2$, without first filtering off the white precipitate which is produced. Filter; pass the gas again through the clear filtrate, to make sure that the metals have been entirely precipitated. Wash the precipitate with hot water; remove a portion from the filter; boil with a little $\mathbf{S}Am_2$, and filter off. A black residue is left, consisting of $\mathbf{Hg}S$, $\mathbf{Pb}S$, $\mathbf{Bi}_2S_3$, $\mathbf{Cu}S$, $\mathbf{Cd}S$. The solution contains $\mathbf{As}_2S_3$, $\mathbf{Sb}_2S_3$, $\mathbf{Sn}S$, and $\mathbf{Sn}S_2$ dissolved by the $\mathbf{S}Am_2$. This can be shown by acidulating with dilute hydrochloric acid, when a yellow precipitate comes down—because yellow ammonic sulphide converts $\mathbf{Sn}S$ into $\mathbf{Sn}S_2$—consisting of the sulphides of As, Sb, Sn.

This shows that *we can divide Group II by means of ammonic sulphide, into two portions.*

The name *sulphide*, in its widest sense, is given to all compounds into which sulphur enters as the electronegative or chlorous element. A remarkable analogy is observable between oxides and sulphides.

There is a certain class of sulphides which resemble metallic oxides or bases; another class which plays the part of oxy-acids. Sulphides are therefore divided into *sulpho-bases* and *sulpho-acids*. To the latter belong the sulphides of H, As, Sn, Sb (Pt, Au); to the former the sulphides of many metals, especially such of the metals as constitute powerful bases (K, Na, Am, Ba, Ca, etc.) An electropositive or basylous element, which forms with oxygen an oxygen compound, combines generally also with the same number of sulphur atoms, to form a corresponding *sulphur* compound, in which the sulphur is almost invariably a dyad.

The resemblance in the constitution of these oxygen and sulphur compounds is further borne out by the analogy in their solubility and alkaline reaction. Thus we have—

Oxy-bases.		*Sulpho-bases.*	
$\mathbf{O}K_2$	Potassa, alkaline and soluble.	$\mathbf{S}K_2$	Potassic sulphide, alkaline and soluble.
$\mathbf{O}Am_2$	Ammonia „ „	$\mathbf{S}Am_2$	Ammonic „ „
$\mathbf{O}Na_2$	Soda „ „	$\mathbf{S}Na_2$	Sodic „ „
$\mathbf{Ba}O$	Baryta „ „	$\mathbf{Ba}S$	Baric „ „
$\mathbf{Ca}O$	Lime „ „	$\mathbf{Ca}S$	Calcic „ „
$\mathbf{Fe}O$	Ferrous oxide, no reaction, insoluble.	$\mathbf{Fe}S$	Ferrous „ no reaction, insoluble.
$\mathbf{Zn}O$	Zincic „ „	$\mathbf{Zn}S$	Zincic „ „

Oxy-anhydrides.		*Sulpho-anhydrides.*	
$\mathbf{As}_2O_3$	Arsenious anhydride.	$\mathbf{As}_2S_3$	Arsenious sulphide, or sulpharsenious anhydride.
$\mathbf{As}_2O_5$	Arsenic „	$\mathbf{As}_2S_5$	Arsenic sulphide, or sulpharsenic anhydride.
$\mathbf{Sb}_2O_3$	Antimonious „	$\mathbf{Sb}_2S_3$	Antimonious sulphide, or sulphantimonious anhydride.
$\mathbf{Sb}_2O_5$	Antimonic „	$\mathbf{Sb}_2S_5$	Antimonic sulphide, or sulphantimonic anhydride.
$\mathbf{Sn}O_2$	Stannic „	$\mathbf{Sn}S_2$	Stannic sulphide, or sulphostannic anhydride.

Oxy-acids.		*Sulpho-acids.*	
$\mathbf{As}Ho_3$	Arsenious acid.	$\mathbf{As}Hs_3$	Sulpharsenious acid.
$\mathbf{As}OHo_3$	Arsenic acid.	$\mathbf{As}SHs_3$	Sulpharsenic acid.
$\mathbf{Sb}Ho_3$	Antimonious acid.	$\mathbf{Sb}Hs_3$	Sulphantimonious acid.
$\mathbf{Sb}OHo_3$	Antimonic acid.	$\mathbf{Sb}SHs_3$	Sulphantimonic acid.
$\mathbf{Sb}O_2Ho$	Metantimonic acid.	$\mathbf{Sb}S_2Hs$	Sulphometantimonic acid.
$\mathbf{Sn}Ho_4$	Stannic acid.	$\mathbf{Sn}Hs_4$	Sulphostannic acid.

Sulpho-salts are obtained by the mutual action of a sulpho-acid and a sulpho-base upon each other.

Sulphides soluble in water, comprising the sulphides of the alkalies and alkaline earthy metals, are divided into *normal sulphides*, such as $\mathbf{S}K_2$, $\mathbf{S}Am_2$, $\mathbf{S}Na_2$, $\mathbf{Ba}S$; into *sulphhydrates* (acid sulphides), such as $\mathbf{S}KH$, $\mathbf{S}AmH$, $\mathbf{Ba}Hs_2$; and *polysulphides*, such as $\mathbf{S}_2H_2$, $\mathbf{S}_5K_2$, $\mathbf{S}_5Am_2$. The aqueous solutions of the normal and acid sulphides are colourless, and give off $\mathbf{S}H_2$ when treated with dilute hydrochloric acid, *without separation of sulphur*. Solutions of the polysulphides are yellow, or yellowish brown, and when treated with hydrochloric acid, give off sulphuretted hydrogen, with separation of white (or precipitated) sulphur. The number of sulpho-salts is small compared with the salts of oxy-acids, and they are far less stable than ordinary oxy-salts. This arises from the fact that sulphur is comparatively indifferent to chlorine, phosphorus, nitrogen, carbon, silicon—non-metallic elements which are endowed with a powerful chemical affinity for oxygen, with which they form in the presence of water energetic oxy-acids—and that there are either no sulphides corresponding to the oxygen compounds of these elements, or sulphides of a very indifferent nature. The number of sulpho-acids is principally restricted to the acids enumerated above, and these again combine mostly only with the soluble sulphides possessed of an *alkaline reaction;* or, if combined with the sulphides of the heavy metals, as in certain minerals, they are readily decomposed by chemical agencies.

The following is a list of some of the more important sulpho-salts compared with the corresponding oxy-salts:—

Oxy-salts.		*Sulpho-salts.*	
$\mathbf{Sn}\mathrm{Nao}_2$	Disodic stannite.	$\mathbf{Sn}\mathrm{Nas}_2$	Disulphosodic sulphostannite.
$\mathbf{Sn}\mathrm{ONao}_2$	Disodic stannate.	$\mathbf{Sn}\mathrm{SNas}_2$	Disulphosodic sulphostannate.
$\mathbf{As}\mathrm{Ko}_3$	Tripotassic arsenite.	$\mathbf{As}\mathrm{Ks}_3$	Trisulphopotassic sulpharsenite.
$\mathbf{As}\mathrm{ONao}_3$	Trisodic arseniate.	$\mathbf{As}\mathrm{SNas}_3$	Trisulphosodic sulpharseniate.
$\mathbf{Sb}\mathrm{OKo}$	Potassic metantimonite.	$\mathbf{Sb}\mathrm{SKs}$	Sulphopotassic metasulphantimonite.
$\mathbf{Sb}\mathrm{O_2Ko}$	Potassic metantimoniate.	$\mathbf{Sb}\mathrm{S_2Ks}$	Sulphopotassic metasulphantimoniate.

In these sulphur compounds the radical Nas, sodiumsulphyl, occupies the place of the compound radical Nao, sodoxyl. In like manner

Ks	Potassiumsulphyl	occupies the place of	Ko	Potassoxyl.
Ams	Ammoniumsulphyl	„	Amo	Ammonoxyl.
Bas''	Bariumsulphyl	„	Bao''	Baroxyl.
Cas''	Calciumsulphyl	„	Cao''	Calciumoxyl,

in the analogous sulpho-salts.

Instances of some interesting natural sulpho-salts, to be considered more fully under silver and lead, are:—

$\mathbf{As}\mathrm{Ags}_3$ trisulphargentic sulpharsenite (*proustite*).

$\mathbf{Sb}\mathrm{Ags}_3$ trisulphargentic orthosulphantimonite (*pyrargyrite* or *dark red silver ore*).

$\mathbf{Sb}_2\mathrm{S}''(\mathrm{Cu_2FeS}''_3)_2''$ sulphocuproso ferrous pyrosulphantimonite (*fahl ore*).

$\mathbf{Sb}_2\mathrm{Pbs}''_3$ trisulphoplumbic orthosulphantimonite (*boulangerite*).

$\mathbf{Sb}_2\mathrm{Pbs}''_2(\mathrm{Cu_2S}''_2)''$ disulphoplumbic sulphocuprous orthosulphantimonite (*bournonite*).

$\mathbf{Sb}_4\mathrm{S_3Pbs}''\mathrm{Pbs}''_2$ trisulphoplumbic metasulphantimonite[*] (*jamesonite*).

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[*] This compound may also be viewed as $\mathbf{Sb}_2\mathrm{S_2Pbs}''$ (sulphoplumbic metasulphantimonite) and $\mathbf{Sb}_2\mathrm{SPbs}''_2$ (sulphoplumbic pyrosulphantimonite).

Treat another portion of the above $\mathbf{S}H_2$ precipitate with NaHo or KHo and filter off. A black residue is likewise left, and on adding dilute HCl to the filtrate, $\mathbf{As}_2S_3$, $\mathbf{Sb}_2S_3$, $\mathbf{Sn}S$ and $\mathbf{Sn}S_2$ are reprecipitated.

This shows that the *hydrates of the alkali metals dissolve a portion of the sulphides precipitated by* $\mathbf{S}H_2$ *in Group II.* The following equations explain the action of the alkaline hydrates:—

$\mathbf{Sb}_2S_3$	+ 6KHo =	$\mathbf{Sb}\mathrm{Ks}_3$	+ $\mathbf{Sb}\mathrm{Ko}_3$	+ $3\mathbf{O}H_2$.
Antimonious sulphide.		Trisulphopotassic sulphantimonite.	Tripotassic antimonite.	
$\mathbf{As}_2S_3$	+ 4KHo =	$\mathbf{As}\mathrm{HsKs}_2$	+ $\mathbf{As}\mathrm{HoKo}_2$	+ $\mathbf{O}H_2$.
Arsenious sulphide.		Sulphhydric disulphopotassic sulpharsenite.	Hydric dipotassic arsenite.	
$2\mathbf{Sn}S$	+ 4KHo =	$\mathbf{Sn}\mathrm{Ks}_2$	+ $\mathbf{Sn}\mathrm{Ko}_2$	+ $2\mathbf{O}H_2$.
Stannous sulphide.		Disulphopotassic sulphostannite.	Dipotassic stannite.	
$2\mathbf{Sn}S_2$	+ 4NaHo =	$\mathbf{Sn}S''\mathrm{Nas}_2$	+ $\mathbf{Sn}O\mathrm{Nao}_2$	+ $\mathbf{O}H_2$ + $\mathbf{S}H_2$.
Stannic sulphide.		Disulphosodic sulphostannate.	Disodic stannate.	

Addition of hydrochloric acid reprecipitates the sulphides, thus:—

$$\mathbf{Sb}\mathrm{Ks}_3 + \mathbf{Sb}\mathrm{Ko}_3 + 6HCl = \mathbf{Sb}_2S_3 + 6KCl + 3\mathbf{O}H_2.$$

Hence the metals which are precipitated by $\mathbf{S}H_2$ in Group II, can be subdivided by means of $\mathbf{S}\mathrm{Am}_2$ or NaHo into—

A. *Metals whose sulphides act as sulpho-bases*, viz., the sulphides of Hg, Pb, Bi, Cu and Cd. These are insoluble in ammonic sulphide ($\mathbf{Hg}S$ dissolves to some extent in potassic or sodic sulphide; $\mathbf{Cu}S$ is somewhat soluble in ammonic sulphide).

B. *Metals whose sulphides act as sulpho-acids*, viz., the sulphides of As, Sb, Sn (Au, Pt).

GROUP II. SUBDIVISION A.

1. **MERCURY.** Hg''.—Occurs native, but is chiefly obtained from *cinnabar* or mercuric sulphide, $\mathbf{Hg}S$.

EXAMINATION IN THE DRY WAY.

Add a little finely-divided lead or zinc to a few globules of mercury on a watch-glass. The liquid metal mercury becomes thick and pasty by the combination with the solid metal lead or zinc. It enters into combination with the lead, in the cold, to form an *amalgam*. Other metals combine with mercury only when heated.

The term amalgam is applied to the combinations into which mercury enters with other metals. Combinations between metals, other than mercury, are called *alloys*. This property of mercury has received an important application in the extraction of gold and silver from poor ores by the so-called *amalgamation process.* Mercury can be separated again by distillation, gold and silver being left behind.

The combination of the metal mercury with other metals is obviously due to its liquid condition at the ordinary temperature, which facilitates its being brought into intimate contact with other metals. This contact action is materially increased, if the solid metals are offered to the mercury in a finely-divided condition, or in the form of foil—an amalgam of 4 parts of tin and 1 part of mercury is employed for covering looking-glasses—and by rubbing the two metals together in a mortar.

Heat some *cinnabar* in a small flask with narrow neck, loosely closed with a piece of charcoal. $\mathbf{Hg}S$ sublimes without undergoing any chemical change.

Heat a little *cinnabar* in a piece of glass tube open at both ends, and allow a current of air to pass over it. Hg is seen to condense in the form of a metallic mirror towards the further end of the tube, and $\mathbf{S}O_2$ makes itself perceptible by its odour.

Heat about two parts of yellow mercuric oxide, $\mathbf{Hg}O$, and one part of mercuric sulphide, $\mathbf{Hg}S$, in a test tube. Metallic mercury sublimes and sulphurous anhydride is given off, according to the equation :—

$$\mathbf{Hg}S + 2\mathbf{Hg}O = Hg_3 + \mathbf{S}O_2.$$

Introduce some *cinnabar* into a small tubulated retort connected with a two-necked receiver and gas delivery-tube, and pass through the tubulus of the retort a current of air or oxygen from a gas-holder, and heat gently. A blue flame playing over the $\mathbf{Hg}S$ indicates that combustion takes place. Mercury distils and condenses partly in the neck of the retort and partly in the receiver. Sulphurous anhydride issues from the delivery-tube and is readily recognized by its pungent odour; or it may be passed into water and the solution tested with litmus-paper.

This illustrates the mode of extraction of mercury from its principal ore. *Cinnabar* is roasted in a reverberatory furnace, and proper provision is made for the condensation of the vapour of mercury in chambers and flues. The sulphurous anhydride is allowed to escape.

$\mathbf{Hg}S$ (as well as $\mathbf{S}Ag_2$, $\mathbf{Au}_2S_3$, $\mathbf{Pt}S_2$) parts with its sulphur when roasted in the air, and yields the metal: *it is in fact reduced to the metallic state by oxygen*, owing to the weak affinity which exists between the metal mercury and the non-metal sulphur, and owing likewise to its weak affinity for oxygen, on account of which the $\mathbf{Hg}O$ (and $\mathbf{O}Ag_2$) first formed gives up its oxygen again to a fresh quantity of $\mathbf{Hg}S$ (or $\mathbf{S}Ag_2$).

Hydrogen and carbon, copper, tin, zinc, etc., reduce $\mathbf{Hg}S$ at a high temperature, forming with the sulphur $\mathbf{S}H_2$, $\mathbf{C}S_2$ (carbonic disulphide), $\mathbf{Cu}S$, etc. The native $\mathbf{Hg}S$ is, however, best reduced by the action of strong bases, such as lime or soda.

Mix a little cinnabar with dry $\mathbf{C}ONao_2$, and heat in a little tube, sealed up at one end, or blown into a small bulb. Metallic mercury sublimes and forms a mirror in the cold part of the tube; the sulphur is fixed by the alkali metal.

REACTIONS IN THE WET WAY.

Mercury forms two series of salts: **mercurous and mercuric salts.**

It dissolves readily in nitric acid, even in the cold; forming mercurous nitrate, if the mercury be in excess, and mercuric nitrate, if the acid be in excess. These salts have the composition:—

$$\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}\mathrm{Hg_2o}'' \quad \text{and} \quad \begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}\mathrm{Hgo}''$$

Mercurous nitrate. Mercuric nitrate.

Mercurous salts contain $\mathbf{Hg}_2O$; mercuric salts, $\mathbf{Hg}O$.
Mercurous oxide. Mercuric oxide.

The oxygen atom being in the one case linked to two atoms of the dyad mercury, thus $\left\{\begin{matrix}\mathbf{Hg}\\ \mathbf{Hg}\end{matrix}\right\rangle O$, the mercury atoms being held together by one of their bonds as well as by the bonds of the oxygen atom; in the other to one atom, thus: $\mathbf{Hg}{=}O$.

Mercurous oxide exhibits a tendency to combine with another atom of oxygen, or when exposed to heat, to part with one atom of mercury and to become converted into mercuric oxide. Hence we possess in mercurous salts powerful *reducing* agents.

On account of the *insoluble chloride* which mercurous salts form, we shall consider its reactions in connection with the reactions for silver and lead in Group I.

In order to study the reactions of mercuric salts, we can either employ A SOLUTION OF MERCURIC NITRATE, $\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}\mathrm{Hgo}''$, or MERCURIC CHLORIDE, $\mathbf{Hg}Cl_2$ (*corrosive sublimate*).

$\mathbf{S}H_2$ (**group-reagent**) added to $\mathbf{Hg}Cl_2$ gives a *black* precipitate of **mercuric sulphide**, $\mathbf{Hg}S$. The precipitation is marked by characteristic changes of colour. Accordingly as sulphuretted hydrogen water is added in small quantities, or the gas passed slowly through the solution, it produces at first a perfectly *white* precipitate, and on the addition of more $\mathbf{S}H_2$, a *yellow* precipitate which passes through *dirty yellow* to *brown* and becomes *black* only when excess of $\mathbf{S}H_2$ has been added to the mercuric salt. The white, yellow or brown precipitate consists of varying quantities of $\mathbf{Hg}S$ and $\mathbf{Hg}Cl_2$. It may be represented by the formula $\left\{\begin{matrix}\mathbf{Hg}Cl\\ S''\\ \mathbf{Hg}Cl\end{matrix}\right.$ (**dimercuric sulphodichloride**). $\mathbf{Hg}S$ is insoluble in nitric or hydrochloric acid and in ammonic sulphide, potassic hydrate or potassic cyanide; soluble, however, in aqua regia and in potassic or sodic sulphide, in presence of sodic hydrate.

$\mathbf{S}Am_2$ gives the same precipitate.

NaHo or KHo added in excess produces a *yellow* precipitate of **mercuric oxide**, $\mathbf{Hg}O$, insoluble in excess, unless the mercuric solution contains much free acid.

AmHo produces a *white* precipitate of **mercuric salt** and **mercuramide**, known as the "*white precipitate.*"

$$\begin{pmatrix} H_2 \\ \mathbf{N}_2H_2 \\ Hg'' \end{pmatrix} + \mathbf{H}gCl_2 = 2(\mathbf{N}H_2Hg''Cl).$$

Mercurammonic
chloride.

$\mathbf{C}ONao_2$ or $\mathbf{C}OKo_2$ gives a *reddish brown* basic precipitate.

KI gives a *bright red* precipitate of **mercuric iodide**, $\mathbf{H}gI_2$, soluble either in excess of potassic iodide or of the mercuric salt. $\mathbf{H}gI_2$ as well as $\mathbf{H}gCl_2$ sublime unchanged.

KCy gives with mercuric nitrate (not the chloride) a *white* precipitate of **mercuric cyanide**, $\mathbf{H}gCy_2$, soluble in excess; not decomposed by boiling with alkalies or alkaline carbonates, but only by $\mathbf{S}H_2$.

Mercuric salts are readily reduced to mercurous salts :—

$\mathbf{S}nCl_2$ (**stannous chloride**) gives with mercuric salts a *white* precipitate of **mercurous chloride**, $\mathbf{H}g_2Cl_2$, which when boiled with excess of the reagent, is reduced to grey metallic mercury. On pouring off the solution and boiling the grey precipitate with HCl, the mercury is obtained in little globules.

$\mathbf{S}O_2Feo''$ (**ferrous sulphate**) reduces $\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Hgo''$, but not $\mathbf{H}gCl_2$, to the metallic state.

Cu, Zn, Fe precipitate metallic mercury from mercuric solutions, provided they are not too acid.

Mercuric salts act the part of *oxidizing agents :* they are first reduced to mercurous salts, and finally to metallic mercury.

QUESTIONS AND EXERCISES.

1. What is understood by the terms *sulpho-base*, *sulpho-acid*, *sulpho-salt ?*
2. Define normal sulphides, sulphhydrates, and polysulphides, and state how they can be distinguished by treatment with HCl.
3. Give instances of sulpho-salts together with the corresponding oxy-salts.
4. Write out the graphic formulæ of a few sulpho-salts and of the minerals *boulangerite*, *jamesonite*, *fahl ore*.
5. Which metals form sulphides capable of acting as sulpho-acids, and which form basylous sulphides ?
6. Write out the formulæ, both symbolic and graphic, for the persulphides of the metals K, Na, Ba, Ca, Fe.
7. What changes take place when the sulphides of As, Sb, and Sn are boiled, 1st, with $\mathbf{S}Am_2$, 2nd, with NaHo ? Express the changes by equations.
8. Give the graphic formulæ of cinnabar, dimercuric sulpho-dichloride, of *white precipitate* and of mercuric nitrate.
9. Write out the symbolic equations for the reactions which mercuric nitrate gives with the group and special reagents.
10. Calculate the percentage composition of *white precipitate*.
11. How much metallic copper will have to be dissolved, in order to precipitate 2 grms. of Hg from a solution of mercuric chloride ?
12. Explain why the dyad condition appertains to one atom of mercury and to the double atom. Give proofs of the atomicity of mercury in mercurous and mercuric compounds.
13. How is *corrosive sublimate* manufactured, and whence does it derive its name ?

14. 1·5 grm. of $\mathrm{HgCl_2}$ is precipitated as HgS and collected on a weighed filter. How much by weight of HgS should there be obtained?
15. *Cinnabar* is sometimes found adulterated with red lead, red oxide of iron, brick-dust. State how you would discover the adulteration. (No separation of the impurities from each other is required.)
16. What reaction takes place when mercury is acted upon by concentrated sulphuric acid? and by what consecutive stages is the product of this reaction converted into *white precipitate*?
17. How much metallic mercury will 100 lbs. of *cinnabar* yield when distilled with lime?
18. What is the percentage composition of an amalgam containing $\mathrm{Sn_4Hg}$?

2. **LEAD**, Pb'' and $^{\text{iv}}$—Only a slight precipitate of PbS is for the most part obtained in Group II, since the greater part of the lead is removed in Group I as $\mathrm{PbCl_2}$. It happens frequently that this small quantity of lead is not precipitated by $\mathrm{SH_2}$, on account of the solution being too acid (HCl) or too concentrated, in which case a little lead is found in Group III, and is often mistaken for some other metal. It is necessary therefore to dilute a portion of the filtrate from Group II considerably and to pass a current of $\mathrm{SH_2}$ through, in order to make sure of the presence of lead, especially so, when lead has been discovered in Group I; and, if a precipitate be obtained, to pass the gas once more through the whole of the filtrate, after having diluted it considerably with distilled water.

3. **BISMUTH**, Bi''' and $^{\text{v}}$.—This metal is principally found native; also in combination with oxygen and sulphur, as *bismuth ochre*, $\mathrm{Bi_2O_3}$, from the decomposition of *bismuth glance*, $\mathrm{Bi_2S_3}$, and in the form of sulpho-salts, as *kobellite*, $\mathrm{Bi_2Pbs''_3}$ (trisulphoplumbic orthosulpho-bismuthite), and as *needle ore*, $\mathrm{Bi_2Pbs''_2}\,(\mathrm{'Cu'_2S_2})''$ disulphoplumbico-cuprous orthosulpho-bismuthite.

EXAMINATION IN THE DRY WAY.

The metal bismuth fuses with ease, both in the reducing and oxidizing flame of the blowpipe, covering the charcoal with an incrustation of oxide, **orange yellow**, *while hot*, **lemon yellow**, *when cold*, passing at the edges into a **bluish white**. The incrustation can be driven from place to place by either flame, *without colouring* the outer flame. (DISTINCTION FROM LEAD). Heated with borax or microcosmic salt, $\mathrm{Bi_2O_3}$ gives beads which are *yellowish*, when hot, and *colourless*, when cold. All bismuth compounds can be reduced to the metallic state by heating on charcoal with $\mathrm{CONao_2}$, in the inner or reducing flame. The metallic bead is brittle. (DISTINCTION FROM LEAD and SILVER BEADS). The incrustation is *yellow*.

EXAMINATION IN THE WET WAY.

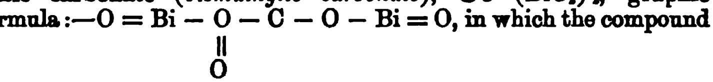
Bismuth dissolves readily in nitric acid, forming $\mathrm{N_3O_6Bio'''}$. A SOLUTION OF THIS SALT IS CONVENIENTLY EMPLOYED.

SH_2 (**group-reagent**) gives a *brownish black* precipitate of **bismuthous sulphide**, Bi_2S_3, insoluble in alkalies and in alkaline sulphides; soluble in concentrated nitric acid.

Alkaline sulphides give the same precipitate.

KHo, NaHo, and AmHo produce a *white* precipitate of **bismuthous hydrate**, $BiHo_3$, insoluble in excess; on boiling it turns yellow, *i.e.*, it becomes anhydrous (Bi_2O_3).

$COAmo_2$ or $CONao_2$ throws down a *white bulky* precipitate of **basic carbonate** (*bismuthylic carbonate*), $CO(BiO_2)'_2$, graphic formula:—



$$O = Bi - O - \underset{\underset{O}{\|}}{C} - O - Bi = O$$

in which the compound radical **bismuthyl**, BiO, acts the part of H in Ho. The precipitate is insoluble in excess.

$Cr_2O_5Ko_2$ gives a *yellow* precipitate of **basic chromate** $\left\{\begin{array}{l}CrO_2(BiO_2)'\\ O\\ CrO_2(BiO_2)'\end{array}\right.$ readily soluble in dilute nitric acid, insoluble in potassic hydrate. (DISTINCTION FROM PLUMBIC CHROMATE.)

SO_2Ho_2 gives no precipitate. (DISTINCTION FROM LEAD.)

KI produces a *brown* precipitate of **bismuthous iodide**, BiI_3, soluble in excess.

KCy produces a *white* precipitate, insoluble in excess, soluble in acids.

Bismuthous salts are partially decomposed by *water*, a basic salt being precipitated. The addition of free acid redissolves the precipitate. This constitutes the most characteristic reaction for bismuthous salts. The salt most readily precipitated is the chloride ($BiCl_3$). It can be prepared from the nitrate by precipitating the oxide first, and then filtering and dissolving the precipitate off the filter with dilute hydrochloric acid. Excess of acid should be avoided.

OH_2 gives with $BiCl_3$ a *white* precipitate of **bismuthous oxychloride**, BiOCl, which is almost absolutely insoluble in water, but soluble in hydrochloric acid, from which it is reprecipitated on the addition of ammonic or sodic chloride. BiOCl is insoluble in tartaric acid. (DISTINCTION FROM ANTIMONY.)

Metallic zinc precipitates bismuth from its salts.

Bismuthous salts exhibit a tendency to form basic salts, showing that Bi_2O_3 is a very indifferent and weak base.

There are several other oxides known, *e.g.*, **bismuthic oxide** or **anhydride**, Bi_2O_5, which parts readily with two atoms of oxygen, when acted upon by heat or reducing agents.

QUESTIONS AND EXERCISES.

1. How can Bi be separated from Ag, Pb, or Hg?
2. Express in symbolic equations the reactions which a bismuthous salt gives with different reagents in the wet way.
3. Give the graphic formulæ for bismuthous nitrate, bismuthous oxide, *bismuth glance*, bismuthous oxychloride.

4. Calculate the percentage composition of an alloy of
1 atom of Pb,
1 atom of Sn, and
3 atoms of Bi.

5. 1·245 grm. of $\mathbf{Bi}_2O_3$ are obtained from 10 c.c. of a solution of normal bismuthous nitrate. How much metallic bismuth does a litre of the bismuth solution contain?

4. **COPPER**, Cu″.—This metal is found native; also in combination with OXYGEN and SULPHUR, as *red copper ore* or *ruby ore*, $\mathbf{Cu}_2O$, as *vitreous copper* or *copper glance*, $\mathbf{Cu}_2S$, and *indigo copper* or *blue copper*, $\mathbf{Cu}S$; more frequently as *copper pyrites* $\left\{\begin{matrix}\mathbf{Fe}S\\ \mathbf{Fe}S\end{matrix}\right.(Cu_2S_2)''$, (diferric cuprous tetrasulphide), and *variegated copper* or *horseflesh ore*, $\left\{\begin{matrix}\mathbf{Fe}\\ \mathbf{Fe}\end{matrix}\right.(Cu_2S_2)''_3$, (diferric tricuprous hexasulphide); also as *fahl ore*, *bournonite*, etc.; in combination with CARBONIC ACID, as basic carbonate, *malachite*, $\mathbf{C}O\ (OCuHo)'_2$, and *azurite*, *mountain blue*, or *copper azure*, $\begin{matrix}\mathbf{C}HoCuo''\\ \mathbf{C}HoCuo''\end{matrix}Cuo''$; with SULPHURIC ACID, as *blue vitriol*, $\mathbf{S}O_2Cuo'', 5\mathbf{O}H_2$; with PHOSPHORIC ACID, as *phosphorocalcite*, *libethenite*; with ARSENIOUS ACID, as *tennantite*; SILICIC ACID, as *dioptase*, and others.

EXAMINATION IN THE DRY WAY.

Copper minerals form a very numerous class of ores; and as many of them exhibit precisely similar blowpipe reactions, a knowledge of their physical character is indispensable to enable the student to distinguish readily between them. It is advisable to examine the doubtful ores in the wet way also.

The most characteristic reaction in the dry way is that which copper compounds give, when heated in a bead of borax or microcosmic salt before the blowpipe flame. The bead is **green** *whilst hot*, **blue** *on cooling*. (Comp. Exp. 89.) Most copper compounds, when heated on platinum wire in the inner flame, impart an **intense green** colour to the outer flame. All copper compounds are reduced when heated in the inner flame on charcoal, together with $\mathbf{C}ONao_2$ and KCy, yielding red metallic scales. Sulphides give off $\mathbf{S}O_2$, when roasted in an open tube, and leave $\mathbf{Cu}O$ behind. *Malachite* or *azurite* gives off water and carbonic anhydride when gently heated in a tube. Blue vitriol loses water, sulphurous anhydride and oxygen, and leaves cupric oxide. Cupric phosphate, arseniate, and silicate fuse to coloured glasses.

Metallic copper is not affected in the dry air at the ordinary temperature, but is readily oxidized when heated in air or oxygen (comp. Exp. 16) and converted into black cupric oxide. Hydrochloric acid dissolves copper but slightly, forming $\mathbf{Cu}_2Cl_2$; nitric acid is the most active solvent for copper (as it is for Ag, Hg, Pb.

and Bi), forming cupric nitrate (comp. Exp. 67). Sulphuric acid (concentrated) dissolves copper, on heating, with evolution of $\mathbf{S}O_2$, and formation of $\mathbf{S}O_2Cuo''$ (comp. Exp. 64).

$\mathbf{S}O_2Ho_2$ acts here the part of an oxidizing agent. This method of preparing sulphurous anhydride gas is frequently employed in the laboratory in preference to other methods.

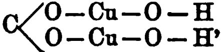
EXAMINATION IN THE WET WAY.

A SOLUTION OF CUPRIC SULPHATE, $\mathbf{S}O_2Cuo''$, OR CUPRIC NITRATE, $\begin{array}{l}\mathbf{N}O_2\\ \mathbf{N}O_2\end{array}Cuo''$, may conveniently be employed.

$\mathbf{S}H_2$ **(group-reagent)** gives a *brownish black* precipitate of **cupric sulphide,** $\mathbf{Cu}S$, insoluble in dilute sulphuric or hydrochloric acid; slightly soluble in ammonic sulphide; soluble with decomposition in nitric acid; completely soluble in potassic cyanide; insoluble in sodic sulphide or caustic alkalies. $\mathbf{Cu}S$ is rapidly oxidized to $\mathbf{S}O_2Cuo''$ by exposure to the air; it is insoluble in hot dilute sulphuric acid.

$\mathbf{S}Am_2$ produces the same precipitate, somewhat soluble in excess, especially in yellow ammonic sulphide ($\mathbf{S}_5Am_2$).

NaHo or KHo gives a *light blue* precipitate of **cupric hydrate,** $\mathbf{Cu}Ho_2$. The precipitate turns black on boiling and becomes denser. Three molecules of $\mathbf{Cu}Ho_2$ lose two molecules of $\mathbf{O}H_2$ and leave $3\mathbf{Cu}O,\mathbf{O}H_2$ (graphic formula $H-O-Cu-O-Cu-O-Cu-O-H$). In the presence of many organic substances, such as grape sugar, etc., the precipitate dissolves to a deep blue solution, whence the whole of the copper is reprecipitated on boiling, in the form of *bright red* **cuprous oxide,** $\mathbf{Cu}_2O$.

$\mathbf{C}ONao_2$ produces a *greenish blue* **basic carbonate,** of the composition $\mathbf{C}O\,(OCu''\,Ho)'_2$, graphic formula  $O{=}C\left\langle\begin{array}{l}O-Cu-O-H\\ O-Cu-O-H\end{array}\right.$' carbonic anhydride being evolved. This precipitate is converted on boiling into the black precipitate of $3\mathbf{Cu}O,\ \mathbf{O}H_2$. It is soluble in ammonic hydrate to an azure blue and in potassic cyanide to a colourless fluid forming a soluble double cyanide.

AmHo or $\mathbf{C}OAmo_2$ when added in small quantities, produces a *greenish blue* precipitate of a **basic salt,** which dissolves readily in excess of the reagents, and forms a magnificent *azure blue* liquid,—a blue which is perceptible, if a solution contains small traces of copper only. The blue solution contains a double compound of **cuprammonic hydrate,** $\mathbf{N}_2\left(\begin{array}{l}H_2\\ H_2\\ H_2\\ Cu''\end{array}\right)Ho_2$, **and ammonic sulphate,** or ammonio-cupric sulphate, symbolic formula, $\mathbf{S}Ho_2Amo_2\left[\begin{array}{l}NH_3\\ NH_3\end{array}CuO_2\right]''$, whence the black cupric oxide separates on boiling with sodic hydrate.

This tendency of ammonia to combine with cupric hydrate and to form cuprammonic hydrate induces metallic copper to combine with oxygen even at the *ordinary temperature* (comp. Exp. 100).

KCy gives a *greenish yellow* precipitate of **cupric cyanide**, $CuCy_2$, soluble in excess. SH_2 produces no precipitate from this solution.

K_4FeCy_6 gives a *reddish brown* precipitate of **cupric ferrocyanide**, Cu_2FeCy_6, insoluble in dilute acids, decomposed by potassic or sodic hydrate, with separation of $3CuO, OH_2$. Even in very dilute solutions of copper salts a brownish colour is produced,—best seen when the reaction is performed on a watch glass, placed on a sheet of white paper or in a little porcelain dish. Hence K_4FeCy_6 supplies one of the most delicate reactions for copper salts.

Metallic zinc or iron precipitates metallic copper, especially in the presence of a little free hydrochloric acid. If a few drops of a slightly acidulated dilute copper solution are placed on platinum foil (the lid of a platinum crucible), together with a small piece of sheet zinc, the platinum becomes rapidly coated with a reddish film of metallic copper, visible even in the case of very dilute solutions, an equivalent quantity of the metal zinc being dissolved.

This simple experiment requires some explanation. Bright copper, as we have already seen, is not attacked by dilute hydrochloric or sulphuric acid. Metals such as Pb, Hg, Ag, Au, Pt are also indifferent to dilute hydrochloric or sulphuric acid, whilst zinc and iron are readily dissolved with evolution of hydrogen, the metals taking the place of the hydrogen in two molecules of hydrochloric acid.

By the aid of voltaic electricity, however, we are enabled to dissolve metals in dilute hydrochloric or sulphuric acid, which are either not dissolved at all, such as copper, or dissolve only with difficulty, such as the metal tin. This is done by connecting the positive pole of a voltaic battery with a piece of the metal to be dissolved, and the negative pole with a platinum wire ending in a piece of platinum foil. Both electrodes dip into the dilute hydrochloric or sulphuric acid solutions.

Connect the positive pole, *a*, with a piece of sheet copper or a coil of copper wire, placed in dilute sulphuric acid, contained in a glass basin, as seen in Fig. 76. The negative pole *b*, consisting of a platinum wire fused to a strip of platinum foil, dips likewise into the dilute acid, without touching, however, the copper. The solution turns blue, owing to the formation of a blue cupric salt, and the sheet of metallic copper or the copper wire dissolves after some time. Hydrogen is evolved at the negative pole.

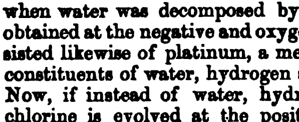


FIG. 76.

This shows that the action of dilute acids upon copper which is nil at the ordinary temperature is very energetic when we call voltaic electricity to our aid.

The reaction will be readily understood, if it be remembered what took place when water was decomposed by voltaic electricity in Exp. 29. Hydrogen was obtained at the negative and oxygen at the positive electrode, because the latter consisted likewise of platinum, a metal which has no affinity for oxygen. Hence both constituents of water, hydrogen and oxygen, were evolved at the respective poles. Now, if instead of water, hydrochloric acid be decomposed in like manner, chlorine is evolved at the positive electrode. If the positive electrode consist, however, of a metal, such as Zn, Cu, Fe, for which chlorine possesses a strong affinity, the latter combines with these metals, the moment it is liberated on the positive electrode, or as it is termed in its nascent state (*in statu nascendi*), and hydrogen alone is evolved at the negative pole.

If in the place of hydrochloric or sulphuric acid, we employ a dilute solution of a metallic chloride or sulphate, ex. gr. cupric sulphate, SO_2Cuo'', and dip the two electrodes into it, we observe at the negative (or platinum) electrode instantaneously a red film or deposit of metallic copper, whilst at the positive (or zinc) electrode, no evolution of gas is visible, since the metallic zinc is acted upon by the acid liberated from the copper, and is converted thereby into $\mathbf{S}O_2Zno''$. An equivalent quantity (65 parts by weight) of zinc remains dissolved in the acid for the 63·5 parts by weight of copper, precipitated on the platinum foil or crucible-lid. In this manner the amount of copper present in a solution may be determined quantitatively. The undissolved zinc and zincic salt are removed and the platinum with its deposit of copper dried and weighed. The total weight, minus the previous weight of the platinum, gives the weight of the metallic copper.

It will be readily perceived that this and other similar experiments furnish valuable illustrations of the atomic theory, and they acquire on this account additional interest.

Great interest attaches, moreover, to these chemical changes, on account of the important practical application which they have found, of late, in covering metals—mostly the common metals—with a thin coating of noble metals (electroplating, silvering, platinizing), or in producing solid metallic deposits on properly prepared matrices, generally consisting of some plastic material, such as plaster of Paris, gutta-percha, etc. *(electrotype process).*

Pass a voltaic current through a solution of cupric chloride, $\mathbf{Cu}Cl_2$, by means of copper electrodes. No chlorine gas is evolved at the positive pole, for it is immediately again fixed by its dissolving an equivalent quantity of copper off the positive copper electrode. The movement of the molecules of chlorine and copper in the solution of cupric chloride cannot be perceived; it is nevertheless proved by the decrease in weight of the positive copper electrode and the increase in weight of the negative copper electrode, and we infer from this that the copper is transferred from the positive to the negative pole, although we cannot see the change. The deposition of metallic copper continues, as long as the positive electrode lasts; and the saline solution in the decomposing vessel retains its original strength thus far unaltered.

If a properly prepared mould or matrix of some object be hung in the metallic solution and connected with the negative pole of a voltaic battery, copper will be slowly but steadily deposited on the mould, as long as the positive pole is connected with a sheet of copper, acting as the positive electrode in the bath. The copper thus precipitated is immediately restored to the bath by the dissolution of a fresh quantity of copper. This mode of depositing copper on moulds or matrices by the aid of voltaic electricity is termed the *electrotype process.*

Employ a solution of argentic nitrate instead of the solution of cupric chloride, and introduce the two copper electrodes into the bath. The negative electrode is speedily covered with silver, and an equivalent quantity of copper, *i.e.*, 63·5 parts by weight, is dissolved from the positive copper electrode, and 216 parts by weight of silver (2 × 108, silver being a monad element) are deposited on the negative copper electrode; and it results from this, that in the place of the silver solution, there must ultimately be left a solution of cupric nitrate. This has found a practical application in the *silvering* (electro-plating) of artistic articles made of an inferior metal.

Copper, like mercury, forms a *lower oxide*, $\mathbf{Cu}_2O$, in which two atoms of Cu are joined by one of their bonds, and are also linked to one atom of oxygen; it is analogous in constitution to the important copper ore, $\mathbf{Cu}_2S$, thus:—

$\left\{\begin{matrix}'\mathbf{Hg}'\\'\mathbf{Hg}'\end{matrix}\right.O$	$\left\{\begin{matrix}'\mathbf{Cu}'\\'\mathbf{Cu}'\end{matrix}\right.O$	$\left\{\begin{matrix}'\mathbf{Cu}'\\'\mathbf{Cu}'\end{matrix}\right.S$
Mercurous oxide.	Cuprous oxide (*red copper ore*).	Cuprous sulphide. (*copper glance*).

Cuprous oxide is a feeble base; it forms with concentrated hydrochloric acid cuprous chloride, $\mathbf{Cu}_2Cl_2$, which is colourless when pure. Other acids decompose it into metallic copper and cupric oxide, which latter remains dissolved in the acid as a cupric salt. Cuprous chloride attracts oxygen very rapidly, and is, therefore, a powerful reducing agent.

To A SOLUTION OF CUPROUS CHLORIDE, $\mathbf{Cu}_2Cl_2$, in concentrated hydrochloric acid, add—

$\mathbf{O}H_2$, a *white* precipitate of $\mathbf{Cu}_2Cl_2$ is produced.

KHo gives a *yellow* precipitate of **cuprous hydrate**, $\mathbf{Cu}_2Ho_2$, insoluble in excess; it attracts oxygen very rapidly, being converted into cupric hydrate.

KI, in the presence of $\mathbf{S}OHo_2$, or $\mathbf{S}O_2Feo''$, precipitates from cupric salts *greenish white* **cuprous iodide**, $\mathbf{Cu}_2I_2$, soluble in excess. Both sulphurous acid and ferrous sulphate are reducing agents, which, by the absorption of oxygen from the cupric salt, are converted into $\mathbf{S}O_2Ho_2$ and $\mathbf{S}_2O_6Fe_2o^{vi}$, thus:—

$$(1)\quad \underset{\substack{\text{Cupric}\\ \text{sulphate.}}}{2\mathbf{S}O_2Cuo''} + 2\mathbf{S}O_2Feo'' = \underset{\substack{\text{Cuprous}\\ \text{sulphate.}}}{\mathbf{S}O_2Cu_2o''} + \mathbf{S}_2O_6Fe_2o^{vi}.$$

$$(2)\quad \mathbf{S}O_2Cu_2o'' + 2KI = \underset{\substack{\text{Cuprous}\\ \text{iodide.}}}{\mathbf{Cu}_2I_2} + \mathbf{S}O_2Ko_2.$$

QUESTIONS AND EXERCISES.

1. Show why copper is a dyad element.
2. Express in symbolic equations the reactions of copper in the wet way.
3. Write out the graphic formulæ for *malachite*, *copper glance*, *azurite*, and *blue vitriol*, ammonio-cupric sulphate, cuprous iodide.
4. Explain what takes place—

   1st. When copper is treated with concentrated $\mathbf{N}O_2Ho$.
   2nd. " " " $\mathbf{S}O_2Ho_2$.
   3rd. " " " HCl.
   Give equations.
5. Give instances of the oxidizing action of cupric salts.
6. What action takes place when the polished blade of a knife is plunged into a solution of a cupric salt?
7. How much metallic zinc is required to precipitate 1·5 grm. of copper from a cupric solution?
8. A sample of iron pyrites which has been used for manufacturing sulphuric acid is found on analysis to contain 4·56 per cent. of copper. How much metallic iron is required to precipitate the copper from a hydrochloric acid solution of a ton of the spent pyrites?
9. Explain the electrotype process.
10. What is understood by nascent hydrogen?
11. What is the percentage of metallic copper in *malachite*?
12. How is Cu separated from Ag and Pb?
13. How can copper in $\mathbf{Cu}S$ be separated from bismuth in $\mathbf{Bi}_2S_3$?
14. What change takes place when metallic copper is heated in air?
15. How much hydrogen gas (at 0° and 760 mm. pressure) is required to deprive 10 grms. of ignited cupric oxide of its oxygen, and how much water will be obtained?

5. **CADMIUM**, Cd''.—This metal is found in nature associated with zinc, in certain zinc ores, *e.g.*, *zinc blende*, ZnS. It is of comparatively rare occurrence: only one mineral of cadmium being known at present, viz., the extremely rare *greenockite*, CdS. It can be distilled like mercury or zinc. Being more volatile than metallic zinc, its vapour distils over first, and burns with a brown flame (*brown blaze*), *i.e.*, it is converted into cadmic oxide, CdO.

Cadmium dissolves readily in acids with evolution of hydrogen. It also resembles the metal zinc in being dissolved by boiling potassic hydrate, hydrogen being given off—

$$Cd + 2KHo = CdKo_2 + H_2.$$

EXAMINATION IN THE DRY WAY.

Cadmium compounds, when heated on charcoal in the inner flame, mixed with sodic carbonate, give a characteristic brown incrustation, *i.e.*, they are readily reduced to the metallic state; the metal being highly volatile, is reoxidized on its passage through the outer flame. Cadmium is recognized with more difficulty, when it is in combination with zinc, as for instance in *cadmiferous blende*. By heating, however, a mixture of blende and sodic carbonate and potassic cyanide, for a few moments only, on charcoal, a slight *brown* incrustation is generally obtainable, before the zinc is volatilized. CdO turns the bead of borax or microcosmic salt *yellowish*, whilst hot, *colourless* when cold.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF CADMIC CHLORIDE, $CdCl_2$, or SULPHATE, SO_2Cdo''.

SH_2 **(group-reagent)** gives from dilute solutions a *fine yellow* precipitate of **cadmic sulphide**, CdS, insoluble in alkaline sulphides, caustic alkalies, or potassic cyanide; insoluble in cold, but soluble in hot dilute nitric and hydrochloric acids; soluble also in dilute sulphuric acid. (DISTINCTION FROM COPPER.)

SAm_2, same precipitate.

KHo, a *white* precipitate of **cadmic hydrate**, $CdHo_2$, insoluble in excess.

$AmHo$, same precipitate, soluble in excess.

$COAmo_2$ (free from $AmHo$), a *white* precipitate of **cadmic carbonate**, $COCdo''$, insoluble in excess.

$CONao_2$, same precipitate.

KCy gives a *white* precipitate of **cadmic cyanide**, $CdCy_2$, soluble in excess. Sulphuretted hydrogen precipitates from this solution CdS. (DISTINCTION FROM COPPER.)

Metallic zinc precipitates cadmium from its solutions.

QUESTIONS AND EXERCISES.

1. Describe three methods of separation of Cd from Cu.
2. How is Cd separated from Zn?
3. How is Cd separated from Pb, Ag and Bi?

4. How much cadmic sulphide can be prepared from 10 grms. of crystallised cadmic sulphate, $\mathbf{S}O_2Cdo'', 4\mathbf{O}H_2$?
5. What takes place when *greenockite* is roasted in a glass tube open at both ends?
6. How is the metal cadmium converted 1° into oxide, 2° into chloride, 3° into sulphate?
7. How can we extract cadmium from its oxide or sulphide?
8. You are requested to convert 10 grms. of cadmic sulphate into cadmic bromide; how would you proceed, and how much $\mathbf{Cd}Br_2$ should there be obtained?

SEPARATION OF THE METALS OF SUBDIVISION A, GROUP II, viz., MERCURY, LEAD, BISMUTH, COPPER, CADMIUM, WHOSE SULPHIDES ARE INSOLUBLE IN AMMONIC SULPHIDE OR SODIC HYDRATE.

The precipitate produced by the group-reagent $\mathbf{S}H_2$, which is insoluble in ammonic sulphide or sodic hydrate, may consist of all the five sulphides, or only of one, two, etc. A precipitate of a bright yellow colour, *e.g.*, would be indicative of cadmic sulphide only. If the precipitate be black, it is necessary to examine for all the five metals.

We have already seen that the sulphides of the metals of this subdivision are—

1° insoluble in alkalies and alkaline sulphides, and

2° insoluble in dilute acids, or nearly so; but soluble in concentrated acids.

Concentrated nitric acid dissolves four out of the five sulphides, viz., $\mathbf{Pb}S$, $\mathbf{Bi}_2S_3$, $\mathbf{Cu}S$, and $\mathbf{Cd}S$, with separation of sulphur; mercuric sulphide being soluble only in aqua regia. Hence by boiling with concentrated nitric acid (in the absence of HCl), we can separate mercury from the other metals of subdivision A. We have also seen that concentrated nitric acid converts $\mathbf{Pb}S$ partially into $\mathbf{S}O_2Pbo''$, by the simultaneous oxidation of the sulphur. We should, therefore, obtain in the residue $\mathbf{Hg}S$, as well as $\mathbf{S}O_2Pbo''$ and sulphur. But as the whole of the $\mathbf{Pb}S$ can only be converted into $\mathbf{S}O_2Pbo''$, by boiling with fuming nitric acid, and as $\mathbf{S}O_2Pbo''$ is slightly soluble in concentrated nitric acid, we should not succeed in removing the lead entirely as sulphate. This difficulty is overcome by boiling the whole of the sulphides with moderately concentrated nitric acid, then diluting with water and adding dilute sulphuric acid ($\mathbf{S}O_2Pbo''$ being less soluble in dilute sulphuric acid than in water), and lastly, when cold, adding to the solution its own bulk of alcohol (methylated spirit). A *residue* is left which may be white, indicative of the presence of $\mathbf{S}O_2Pbo''$, or black, from the presence of $\mathbf{Hg}S$ and sulphur. The *solution* contains the metals Bi, Cu, Cd.

EXAMINATION OF THE RESIDUE.—$\mathbf{S}O_2Pbo''$ dissolves readily in certain salts, such as ammonic acetate or tartrate. By treating the residue, therefore, with a concentrated solution of ammonic acetate, we are able to dissolve out the $\mathbf{S}O_2Pbo''$. The absence of mercury compounds may be inferred, if no black but only a yellow residue of sulphur, is left, and if no mercury has been indicated by the reactions in the dry way. The presence of both lead and mercury should, however, invariably be confirmed by special tests; viz., the lead by means of $\mathbf{Cr}O_2Ko_2$, and the mercury, by heating the dry residue in a bulb tube with dry sodic carbonate.

EXAMINATION OF THE SOLUTION.—We have seen that AmHo precipitates $\mathbf{Bi}Ho_3$, which is insoluble in excess, whilst $\mathbf{Cu}Ho_2$ and $\mathbf{Cd}Ho_2$ are likewise precipitated, but are soluble in excess. If a white precipitate be obtained on adding AmHo, we infer that bismuth is present. (Should the lead not have been removed entirely, some $\mathbf{Pb}Ho_2$ would be likewise precipitated.) The precipitate is filtered off and well washed, then redissolved in a little hydrochloric acid, and precipitated by the addition of water. The ammoniacal filtrate is of a fine *azure blue* colour, when copper is present. If colourless, and if, by the addition of $\mathbf{S}H_2$ a fine yellow precipitate comes down, we infer that no copper is present, but only cadmium. If a black precipitate comes down, on passing the gas through the *slightly* acidulated (HCl) solution, we infer the presence of copper and possibly of cadmium. These two metals can be separated either by means of KCy,($\mathbf{Cd}S$ being insoluble in potassic cyanide), or dilute sulphuric acid ($\mathbf{Cu}S$ being insoluble in hot dilute sulphuric acid). Filter again; in the one case copper is left in solution, in the other cadmium. It is not difficult to identify these two metals by special tests.

The separation of the metals mercury, lead, bismuth, copper and cadmium, is therefore based upon:—

1°. *The insolubility of* $\mathbf{Hg}S$ *in nitric acid.*

2°. *The formation of* $\mathbf{S}O_2Pbo''$, *and its solubility in ammonic acetate.*

3°. *The insolubility of* $\mathbf{Bi}Ho_3$ *in excess of ammonic hydrate.*

4°. *The insolubility of* $\mathbf{Cu}S$ *in dilute sulphuric acid, or its solubility in potassic cyanide.*

A tabular scheme for their separation is given in the Analytical Tables, Table II.

PRACTICAL EXERCISES AND QUESTIONS ON GROUP II, SUBDIVISION A, AND THE PREVIOUS GROUPS.

You are requested to analyze—

1. A sample of *galena*, in the dry way only.
2. A hydrochloric acid solution, containing much mercuric and little plumbic chloride.
3. A mixture of the solid salts, blue vitriol, corrosive sublimate, and white vitriol, in the dry and wet way.
4. A mixture of the solid salts, plumbic and bismuthous nitrate, in the dry and wet way.
5. A solution containing much baric chloride and little plumbic chloride.
6. A solution containing cupric, ferrous, and zincic sulphates.
7. A solution of cupric, cadmic, and zincic sulphates, containing ·050 grm. of Cu, ·020 grm. of Cd, and ·500 grm. of Zn.
8. An alloy of zinc and copper (brass).
9. A solution of mercuric, plumbic, and bismuthous nitrates, containing ·050 grm. of Hg, ·500 grm. of Pb, and ·100 grm. of Bi.
10. A sample of *copper glance*, in the dry way only.

11. A sample of *malachite*, in the dry way.
12. A solution of plumbic and bismuthous nitrates (to be distinguished by means of $\mathbf{Cr}O_2Ko_2$ and NaHo).
13. A solution of plumbic and cupric nitrates.
14. What takes place when an ore, containing $\mathbf{Pb}S$, $\mathbf{Cd}S$, and $\mathbf{Zn}S$, is roasted in a current of air?
15. You have given to you a solution of cupric sulphate, dipotassic tartrate, sodic hydrate, and grape sugar; what changes can you produce with these materials?

GROUP II. SUBDIVISION B.

1. **TIN**, Sn'' and ^{iv}.—This metal is found in nature mainly in the form of *tinstone* or *cassiterite*, $\mathbf{Sn}O_2$, sometimes combined with sulphur, as *tin pyrites*, $\mathbf{Sn}S_2$ (*bell-metal ore*).

EXAMINATION IN THE DRY WAY.

When tin minerals are fused on charcoal, with $\mathbf{C}ONao_2$ and KCy, in a strongly reducing flame, they yield small globules of tin which are malleable, and the charcoal becomes covered with a *white* coating of $\mathbf{Sn}O_2$. If this white incrustation be treated with a solution of cobaltous nitrate, and strongly heated, it assumes a *bluish-green* colour, which is characteristic of tin.

By introducing into a borax bead—in which sufficient cupric oxide has been diffused to render the bead faintly blue—*traces* of a tin compound and heating in the reducing flame, the bead turns *reddish brown*, or forms a *ruby-red* glass.

EXAMINATION IN THE WET WAY.

Tinstone being insoluble in acids, must be fused with alkaline carbonates and a reducing agent, such as potassic cyanide, charcoal, or black flux (ignited *Rochelle salt*), when metallic tin is obtained. Tin dissolves slowly in hot hydrochloric acid with evolution of hydrogen and formation of $\mathbf{Sn}Cl_2$, readily in aqua regia with formation of $\mathbf{Sn}Cl_4$. Nitric acid converts tin into metastannic acid, $\mathbf{Sn}_5O_5Ho_{10}$ (see page 84), which by evaporation and ignition is converted into $\mathbf{Sn}O_2$. 100 parts by weight of metallic tin when thus oxidized, are found to increase to 127·6 by weight (atomic weight of $Sn = 118$).

Tin is capable of combining either with two, or four atoms of chlorine, etc. In stannous chloride, $\mathbf{Sn}Cl_2$, the metal exists as a dyad, and in stannic chloride, $\mathbf{Sn}Cl_4$, as a tetrad element. It is capable of forming *two series of salts*, *of oxides*, *sulphides*, etc., viz. :—

Stannous compounds.		*Stannic compounds.*	
$\mathbf{Sn}''Cl_2$	Stannous chloride	$\mathbf{Sn}^{iv}Cl_4$	Stannic chloride
$\mathbf{Sn}''O$	„ oxide	$\mathbf{Sn}^{vi}O_2$	„ oxide (anhydride)
$\mathbf{S}O_2Sno''$	„ sulphate	$\mathbf{Sn}^{vi}S_2$	„ sulphide.
$\genfrac{}{}{0pt}{}{\mathbf{N}O_2}{\mathbf{N}O_2}Sno''$	„ nitrate		
$\mathbf{Sn}''S$	„ sulphide.		

Stannic acid, $SnOHo_2$, combines not only with the strong alkali bases, OK_2, ONa_2, but even with stannous oxide, SnO, to form **stannates**, *e.g.*, $SnOKo_2$, dipotassic stannate, $SnOSno''$, stannous stannate.

A. **Stannous compounds.**—A SOLUTION OF STANNOUS CHLORIDE, $SnCl_2$, is employed.

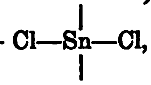
SH_2 (**group-reagent**) gives a *dark brown* precipitate of **stannous sulphide**, SnS, nearly insoluble in normal ammonic sulphide, but readily dissolved by yellow ammonic sulphide, S_2Am_2: from this latter solution it is reprecipitated as yellow stannic sulphide, SnS_2, on the addition of hydrochloric acid; it is also soluble in potassic or sodic hydrate, from which hydrochloric acid precipitates SnS unchanged. Soluble in boiling hydrochloric acid.

SAm_2 gives the same precipitate. Soluble in excess.

KHo or NaHo gives a *white bulky* precipitate of **stannous hydrate**, $SnHo_2$, readily soluble in excess to $SnKo_2$ (dipotassic stannite).

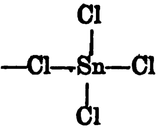
AmHo or $COAmo_2$, same precipitate, insoluble in excess.

By far the most interesting reactions are based, however, upon the tendency of stannous salts to become converted into stannic salts. $SnCl_2$ combines with two more atoms of chlorine to become converted into $SnCl_4$, whereby the chemical affinities of tin for chlorine become satisfied; and stannous compounds may be viewed as unfinished bodies, which can deprive certain other bodies of chlorine, oxygen, etc. Expressed graphically, dyad tin (or *stannosum*, as it is sometimes called) has two bonds left unsatisfied or latent, thus:—



$$\begin{matrix} & | & \\ Cl— & Sn & —Cl \\ & | & \end{matrix}$$

whilst in tetrad tin (*stannicum*) all the bonds are satisfied, thus:—



$$\begin{matrix} & Cl & \\ & | & \\ Cl— & Sn & —Cl \\ & | & \\ & Cl & \end{matrix}$$

or $O{=}Sn{=}O$.

$HgCl_2$ added to a solution of $SnCl_2$ produces first a *white* precipitate of **mercurous chloride**, Hg_2Cl_2, and when boiled with excess of $SnCl_2$, yields a greyish powder of **metallic mercury**.

NO_2Ago gives with excess of $SnCl_2$ a finely divided *black* precipitate of **metallic silver**—

$$2SnCl_2 + 2NO_2Ago = Ag_2 + \begin{matrix}NO_2\\NO_2\end{matrix}Sno'' + SnCl_4.$$

$CuCl_2$ is reduced by $SnCl_2$ to **cuprous chloride**, Cu_2Cl_2, with formation of $SnCl_4$.

Fe_2Cl_6 yields two atoms of chlorine to $SnCl_2$, forming $SnCl_4$, and leaving two molecules of $FeCl_2$. The yellowish solution turns green.

$AuCl_3$ gives with $SnCl_2$ a *purple* precipitate (*purple of cassius*), to which the formula, $SnOAu_2o'' + SnOSno'' + 4Aq$, (sometimes viewed also as $Au_2 + 3SnO_2$), has been assigned. The change may be expressed thus:—

$$2AuCl_3 + 3SnCl_2 + 6OH_2 = Au_2 + 3SnO_2 + 12HCl.$$

This is a most delicate reaction.

B. **Stannic compounds.**—A SOLUTION OF STANNIC CHLORIDE, $\mathbf{Sn}Cl_4$, is employed in studying the reactions of Sn^{iv} in the wet way.

$\mathbf{S}H_2$ (**group-reagent**) gives a *yellow* precipitate of **stannic sulphide**, $\mathbf{Sn}S_2$, readily soluble in alkaline sulphides, potassic hydrate, boiling concentrated hydrochloric acid, and aqua regia; somewhat difficultly soluble in ammonic hydrate and nearly insoluble in ammonic carbonate.

$\mathbf{S}Am_2$, same precipitate, soluble in excess.

KHo or AmHo produces a *white* precipitate of **stannic hydrate**, $\mathbf{Sn}OHo_2$, or **stannic acid**, which is completely soluble in excess, forming dipotassic stannate, soluble in hydrochloric acid.

$\mathbf{CO}Amo_2$ or $\mathbf{CO}Nao_2$ precipitates *white* **stannic acid**, $\mathbf{Sn}OHo_2$, soluble in caustic alkalies.

Stannic chloride furnishes us, moreover, with an interesting process of precipitation, viz., by means of neutral salts, such as sodic sulphate, ammonic nitrate (in fact, most neutral salts). Metastannic acid ($\mathbf{Sn}_5O_5Ho_{10}$) is precipitated on heating, provided the solution of $\mathbf{Sn}Cl_4$ be not too acid, thus:—

$$5\mathbf{Sn}Cl_4 + 20\mathbf{S}O_2Nao_2 + 15\mathbf{O}H_2 = \mathbf{Sn}_5O_5Ho_{10} + 20NaCl + 20\mathbf{S}O_2HoNao.$$

$$5\mathbf{Sn}Cl_4 + 20\mathbf{N}O_2Amo + 15\mathbf{O}H_2 = \mathbf{Sn}_5O_5Ho_{10} + 20AmCl + 20\mathbf{N}O_2Ho.$$

Metallic zinc precipitates from acid solutions of $\mathbf{Sn}Cl_2$ or $\mathbf{Sn}Cl_4$, metallic tin in the form of grey laminæ, or of a spongy mass which can be readily dissolved in hydrochloric acid, especially by the aid of a piece of platinum foil.

Metallic tin or copper reduces $\mathbf{Sn}Cl_4$ to $\mathbf{Sn}Cl_2$, thus:—

$$\mathbf{Sn}Cl_4 + Sn = 2\mathbf{Sn}Cl_2.$$

A solution of $\mathbf{Sn}Cl_2$ (containing hydrochloric acid) cannot be kept when exposed to air, without changing rapidly to $\mathbf{Sn}Cl_4$, on account of the great attraction which stannous salts possess for oxygen, thus:—

$$(1)\ \mathbf{Sn}Cl_2 + O = \mathbf{Sn}O + Cl_2.$$
$$(2)\ \mathbf{Sn}Cl_2 + Cl_2 = \mathbf{Sn}Cl_4.$$
$$(3)\ \mathbf{Sn}O + 2HCl = \mathbf{Sn}Cl_2 + \mathbf{O}H_2.$$

Hence granulated metallic tin or pure tinfoil is usually put into stannous solutions, in order to prevent the formation of $\mathbf{Sn}Cl_4$.

QUESTIONS AND EXERCISES.

1. How do you detect a stannic salt in the presence of a stannous salt?
2. Give the constitutional and graphic formulæ for metastannic and stannic acids, stannous and stannic chlorides.

3. How can the correctness of the atomic weight of tin be shown experimentally?
4. Why does a chemical change take place, when $\mathbf{Sn}Cl_2$ and $\mathbf{Hg}Cl_2$ are heated together?
5. Explain the action of chlorine, nitric acid, and air upon stannous salts.
6. How is Sn separated from Ag?
7. How would you analyze an alloy, consisting of Pb, Cu, Bi, Sn?
8. A *tinstone* yielded on analysis 75·5 per cent. of metallic tin; how much $\mathbf{Sn}O_2$ did it contain?
9. How much chlorine gas by weight and by volume (at 0° and 760 mm.) will be absorbed by 10 grms. of $\mathbf{Sn}Cl_2$?
10. Express in symbolic formulæ the equations for the reactions, in the wet way, of stannous and stannic chlorides.

2. **ANTIMONY**, Sb''' and ^{v}.—This metal is found *native* and in combination with oxygen as *white antimony*, $\mathbf{Sb}_2O_3$, but more frequently as sulphide, $\mathbf{Sb}_2S_3$ (*grey antimony*), and in combination with other metallic sulphides ($\mathbf{Ag}_2S$, $\mathbf{Pb}S$, $'\mathbf{Cu}'_2S$), as sulphantimonite and sulphantimoniate.

EXAMINATION IN THE DRY WAY.

On heating metallic antimony or an antimony mineral, *e.g.*, *grey antimony* with free access of air, either on charcoal or in a glass tube open at both ends, dense white fumes of antimonious and antimonic oxides are given off which condense on the colder part of the charcoal or glass tube, thus:—

$$\mathbf{Sb}_2S_3 + O_9 = \underset{\text{Sublimed.}}{\mathbf{Sb}_2O_3} + 3\mathbf{S}O_2.$$

All compounds of antimony can be reduced to the metallic state when heated on charcoal in the reducing flame, together with $\mathbf{C}ONao_2$ and KCy. A brittle globule of metallic antimony is obtained, giving off dense white fumes of $\mathbf{Sb}_2O_3$ (even after the withdrawal of the metal from the flame), which thickly incrust the metallic globule with a network of brilliant acicular crystals.

EXAMINATION IN THE WET WAY.

Chlorine attacks antimony violently (comp. Exp. 48), forming with it $\mathbf{Sb}Cl_3$ or $\mathbf{Sb}Cl_5$, according to the proportions of chlorine employed, and according to the temperature at which the combination takes place. Hydrochloric acid has scarcely any action upon the metal; aqua regia dissolves it readily to $\mathbf{Sb}Cl_5$. Nitric acid converts it into a compound, containing $\mathbf{Sb}_2O_3$ and $\mathbf{Sb}_2O_5$, insoluble in nitric acid, *soluble in tartaric acid*. *Grey antimony*, $\mathbf{Sb}_2S_3$, as well as $\mathbf{Sb}_2S_5$, dissolve in concentrated hydrochloric acid with evolution of sulphuretted hydrogen, the latter sulphide with separation of sulphur.

Antimony forms two series of compounds by combining either with three, or five atoms of chlorine, etc., viz.:—

Antimonious compounds.		*Antimonic compounds.*	
$\mathbf{Sb}\,Cl_3$,	Antimonious chloride.	$\mathbf{Sb}^vCl_5$,	Antimonic chloride.
$\mathbf{Sb}\,'_2O_3$,	„ oxide.	$\mathbf{Sb}^v{}_2O_5$	„ oxide.
$\mathbf{Sb}\,''_2S_3$,	„ sulphide.	$\mathbf{Sb}^v{}_2S_5$	„ sulphide.
$\mathbf{Sb}'''OHo$	Metantimonious acid.	$\mathbf{Sb}^vO_2Ho$,	Metantimonic acid.[*]

Both these acids can enter into combination with strong bases, such as potassa, or soda, to form weak salts,—metantimonites and metantimoniates, viz.:—

$\mathbf{Sb}'''OKo$,	Potassic metantimonite.
$\mathbf{Sb}^vO_2Ko$,	Potassic metantimoniate.
$\mathbf{Sb}^vO_2Nao$,	Sodic metantimoniate.

$\mathbf{Sb}^vO_2(Sb'''O_2)'$ antimonylic metantimoniate or $\left\{\begin{array}{l}'\mathbf{Sb}^{iv}O_2\\ '\mathbf{Sb}^{iv}O_2'\end{array}\right.$ diantimonic tetroxide, is formed when antimonic oxide (obtained by dissolving antimony in nitric acid) is ignited and is of some importance, as it serves for the quantitative estimation of antimony.

A. **Antimonious compounds.**—A SOLUTION OF ANTIMONIOUS CHLORIDE, $\mathbf{Sb}Cl_3$, is employed for the reactions in the wet way.

$\mathbf{S}H_2$ **(group-reagent)** gives an *orange red* precipitate of **antimonious sulphide**, $\mathbf{Sb}_2S_3$, soluble in alkaline sulphides and in potassic or sodic hydrate; reprecipitated by hydrochloric acid, slightly soluble in ammonic hydrate, insoluble in hydric ammonic carbonate, and in hydric ammonic or hydric potassic sulphites. It dissolves in boiling concentrated hydrochloric acid.

Temperature and concentration of the reagents produce *reciprocal* effects. In a dilute hydrochloric acid solution the $\mathbf{Sb}Cl_3$ exchanges its chlorine in the cold for sulphur, with precipitation of $\mathbf{Sb}_2S_3$, whilst boiling concentrated hydrochloric acid dissolves $\mathbf{Sb}_2S_3$ readily with evolution of $\mathbf{S}H_2$.

$\mathbf{S}Am_2$ produces the same precipitate as $\mathbf{S}H_2$, soluble in excess.

KHo or NaHo precipitates *antimonious oxide*, $\mathbf{Sb}_2O_3$, readily soluble in excess, with formation of potassic antimonite.

AmHo, same precipitate, almost insoluble in excess.

$\mathbf{C}OAmo_2$, $\mathbf{C}OKo_2$, or $\mathbf{C}ONao_2$, same precipitate.

$\mathbf{O}H_2$ decomposes $\mathbf{Sb}Cl_3$, forming a *white insoluble basic salt*, **antimonious oxychloride**, $\mathbf{Sb}OCl$, soluble in tartaric acid. (DISTINCTION FROM BISMUTHOUS OXYCHLORIDE, $\mathbf{Bi}OCl$). Water therefore gives no precipitate with a solution of potassic antimonylic tartrate (*tartar emetic*) $\left\{\begin{array}{l}\mathbf{C}O(Sb'''O_2)'\\ \mathbf{C}HHo\\ \mathbf{C}HHo\\ \mathbf{C}OKo\end{array}\right.$; and alkalies and alkaline carbonates produce a partial precipitation only after some time.

Metallic Zn, Cu, Cd, Fe, Co, Sn, and Pb precipitate the metal in the absence of free nitric acid as a black powder.

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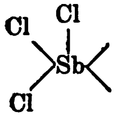
[*] Orthantimonic acid $\mathbf{Sb}OHo_3$, and pyrantimonic acid, $\mathbf{Sb}_2O_3Ho_4$ (said to be formed when antimonic chloride is decomposed by water), are little known.

An exceedingly delicate reaction for antimony consists in precipitating the metal from a dilute hydrochloric acid solution on platinum foil or on the lid of a platinum crucible, by means of a small strip of metallic zinc. H and SbH_3 (antimoniectted hydrogen*) are evolved, and the platinum is stained brown or black by the deposited metal. Mere traces of antimony can thus be discovered. The stain is not affected by cold hydrochloric acid, but disappears on heating with nitric acid. Tin cannot be precipitated on platinum.

Compounds containing triad antimony exhibit a tendency (less marked, however, than in stannous compounds) to combine with more chlorine, etc., and to pass into pentad or antimonic compounds. Expressed graphically—

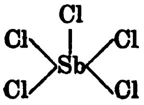
Antimonious chloride



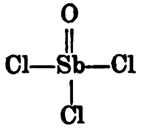
has two bonds left unsatisfied or latent,

whilst pentad antimony in $\mathbf{Sb}^{v}Cl_5$ or $\mathbf{Sb}^{v}OCl_3$ (oxy-trichloride), has all its bonds satisfied, thus:—

Antimonic chloride



Antimonic oxy-trichloride.



The following are some of the reactions naturally arising from this condition of antimonious compounds:—

When a current of chlorine gas is passed over solid $\mathbf{Sb}Cl_2$, a molecule of chlorine is absorbed, and the chloride liquefies, thus:—

$\mathbf{Sb}Cl_3$ + Cl_2 =	$\mathbf{Sb}Cl_5$.
Solid antimonious chloride.	Liquid antimonic chloride.

Sodic metantimonite, $\mathbf{Sb}ONao$, is oxidized, in the presence of sodic hydrate by free iodine, with formation of sodic metantimoniate, $\mathbf{Sb}O_2Nao$, and NaI, thus:—

$$\mathbf{Sb}ONao + I_2 + 2NaHo = \mathbf{Sb}O_2Nao + 2NaI + \mathbf{O}H_2.$$

A hydrochloric acid solution of $\mathbf{Sb}Cl_3$ reduces $\mathbf{Au}Cl$ to metallic gold (frequently with separation of $\mathbf{Sb}O_2Ho$), thus:—

$$3\mathbf{Sb}Cl_3 + 2\mathbf{Au}Cl_3 = 3\mathbf{Sb}Cl_5 + Au_2.$$

Sodic metantimonite is oxidized in an alkaline solution by argentic oxide, $\mathbf{O}Ag_2$, to sodic metantimoniate, argentous oxide, OAg_4, being formed, which is insoluble in ammonic hydrate, $\mathbf{O}Ag_2$ being readily soluble. (DISTINCTION BETWEEN $\mathbf{Sb}_2O_3$ AND $\mathbf{Sb}_2O_5$.)

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* Of this gas more at page 218.

The reactions may be expressed as follows:—

$$(1)\quad \mathbf{Sb}Cl_3 + 4NaHo = \underset{\substack{\text{Sodic}\\ \text{antimonite.}}}{\mathbf{Sb}ONao} + 3NaCl + 2\mathbf{O}H_2.$$

$$(2)\quad 2\mathbf{N}O_2Ago + 2NaHo = \underset{\substack{\text{Argentic oxide,}\\ \text{insoluble in NaHo}\\ \text{(soluble in AmHo).}}}{\mathbf{O}Ag_2} + 2\mathbf{N}O_2Nao + \mathbf{O}H_2.$$

$$(3)\quad \mathbf{Sb}ONao + 2\mathbf{O}Ag_2 = \mathbf{Sb}O_2Nao + \underset{\substack{\text{Black argentous}\\ \text{oxide, insoluble}\\ \text{in AmHo.}}}{OAg_4}.$$

$\mathbf{S}SONao_2$ (**sodic hyposulphite**) reduces antimonious compounds to metallic antimony, which combines with sulphur and forms $\mathbf{Sb}_2S_3$, thus:—

$$3\mathbf{S}SONao_2 + \mathbf{Sb}_2O_3 = \mathbf{Sb}_2S_3 + 3\mathbf{S}O_2Nao_2.$$

B. **Antimonic compounds.**—A SOLUTION OF POTASSIC METANTIMONIATE, $\mathbf{Sb}O_2Ko$, may conveniently be employed for studying the reactions in the wet way.

This salt is prepared by fusing metantimonic acid, $\mathbf{Sb}O_2Ho$, with a large excess of KHo, in a silver crucible, and dissolving the mass in cold water. Fused with caustic soda, a sodic metantimoniate is obtained, which is insoluble in water.

$\mathbf{Sb}O_2Ko$ is readily decomposed by concentrated acids (hydrochloric or nitric), metantimonic acid being precipitated.

$\mathbf{S}H_2$ gives from a solution of $\mathbf{Sb}O_2Ho$ in excess of hydrochloric acid, an orange precipitate of antimonic sulphide, $\mathbf{Sb}_2S_5$, mixed with $\mathbf{Sb}_2S_3$ and S; soluble in alkaline sulphides, readily soluble in ammonic or potassic hydrate; also soluble in boiling concentrated hydrochloric acid, with evolution of $\mathbf{S}H_2$ and deposition of S; only very sparingly soluble in cold hydric ammonic carbonate.

$\mathbf{S}Am_2$, same precipitate, soluble in excess.

$\mathbf{S}O_2Feo''$ does not reduce antimonic compounds.

$\mathbf{N}O_2Ago$, added to an alkaline solution of $\mathbf{Sb}O_2Ko$, yields, for obvious reasons, only $\mathbf{O}Ag_3$, readily soluble in ammonic hydrate.

Antimonic compounds, like stannic salts, *can, under certain conditions, also act as oxidizing agents*, *e.g.*:—

On igniting antimonic anhydride, it splits up into $\mathbf{Sb}_2O_4$ and oxygen.

$\mathbf{Sn}Cl_2$ precipitates $\mathbf{Sb}OHo$ from a hydrochloric acid solution of $\mathbf{Sb}O_2Ho$, the $\mathbf{Sn}Cl_2$ being converted into $\mathbf{Sn}Cl_4$.

On boiling a solution of $\mathbf{Sb}O_2Ho$ in hydrochloric acid with potassic iodide, iodine is liberated, colouring the solution brown. ($\mathbf{Sb}Cl_5$ is in fact frequently employed for the purpose of conveying chlorine to other bodies, both mineral and organic.) Iodine is set free, because $\mathbf{Sb}Cl_5$, on being heated, together with 2KI, forms $\mathbf{Sb}Cl_3 + I_2 + 2KCl$. The liberated iodine is readily recognized by means of starch paste, when the highly delicate and characteristic blue iodide of starch reaction is obtained. (DISTINCTION BETWEEN ANTIMONIOUS AND ANTIMONIC COMPOUNDS.)

QUESTIONS AND EXERCISES.

1. How is antimonious chloride prepared? What change does it undergo when water is added to it?
2. How can the metal antimony be obtained from *grey antimony ore?*
3. By what characteristic reaction can antimony compounds be recognized when examined in the dry way?
4. What is the action of concentrated nitric acid upon metallic antimony? Explain the change by an equation.
5. Explain how $\mathbf{Sb}_2\text{O}_4$ is obtained, and give constitutional and graphic formulæ for it.
6. How can you distinguish between antimonious and antimonic compounds?
7. Explain the action of Zn or Fe upon a solution of $\mathbf{Sb}\text{Cl}_3$.
8. What evidence have we to show the triad and pentad nature of Sb?
9. Give illustrations of the reducing action of antimonious compounds, *e.g.*, antimonious chloride.
10. Give instances of the oxidizing action of antimonic compounds, *e.g.*, metantimonic acid.
11. State how you would separate Sb from Sn, in the wet way.
12. How can Sb be separated from Bi?
13. Express by symbolic equations the reactions for antimony in the wet way.
14. Calculate the percentage composition of *white antimony* and antimonious oxychloride.
15. 1 grm. of a sample of *grey antimony* yielded on analysis ·854 grm. of $\mathbf{Sb}_2\text{O}_4$; what percentage of Sb does the ore contain?
16. How would you separate Sn from Sb, in the dry way?
17. How much $\mathbf{Sb}_2\text{O}_4$ by weight will 1·32 grm. of metallic antimony yield?
18. How much chlorine by weight and by volume (at 0°C. and 760 mm.) is required to convert 10 grms. of $\mathbf{Sb}\text{Cl}_3$ into $\mathbf{Sb}\text{Cl}_5$?
19. How much oxygen gas by weight and by volume (at 0°C. and 760 mm.) can be obtained by igniting 5 grms. of $\mathbf{Sb}_2\text{O}_5$?
20. Describe the preparation of potassic metantimoniate.
21. How much Pb and Sb have to be employed to prepare 50 lbs. of type metal, an alloy having the composition Pb_4Sb?

3. **ARSENIC,** As''' and $^{\text{v}}$.—This body constitutes one of the most widely diffused elements in nature. It is found *native*, but exists most frequently in combination with sulphur as *realgar*, $\left\{\begin{matrix}\mathbf{As}\text{S}'' \\ \mathbf{As}\text{S}''\end{matrix}\right.$, or diarsenious disulphide, and as *orpiment*, $\mathbf{As}_2\text{S}''_3$, or arsenious sulphide (sulpharsenious anhydride); in combination with metals it exists in *arsenical nickel*, $\left\{\begin{matrix}{}''\mathbf{As}' \\ {}''\mathbf{As}'\end{matrix}\right.\text{Ni}$, *copper nickel*, $\left\{\begin{matrix}{}'\mathbf{As}''\text{Ni} \\ {}'\mathbf{As}''\text{Ni}\end{matrix}\right.$, and in *smaltine*, $\left\{\begin{matrix}{}''\mathbf{As}' \\ {}''\mathbf{As}'\end{matrix}\right.\text{Co}$. Arsenic acts in some of these mineral bodies more like a metalloid than a metal. Metallic *arsenides* are frequently found in combination with metallic sulphides, such as the sulphides of Ag, Fe, Ni, Co, Cu, etc., as in the common mineral *mispickel*, or *arsenical pyrites*, $\left\{\begin{matrix}{}''\mathbf{As}' \\ {}''\mathbf{As}'\end{matrix}\right.\text{Fe}''$, $\mathbf{Fe}^{\text{iv}}\text{S}_2$, in *nickel glance* or *grey nickel ore*, $\left\{\begin{matrix}{}''\mathbf{As}' \\ {}''\mathbf{As}'\end{matrix}\right.\text{Ni}''$, $\mathbf{Ni}^{\text{iv}}\text{S}_2$, and in *cobalt glance* $\left\{\begin{matrix}{}''\mathbf{As}' \\ {}''\mathbf{As}'\end{matrix}\right.\text{Co}''$, $\mathbf{Co}^{\text{iv}}\text{S}_2$. Arsenic occurs also in the form of metallic *arseniates*, such

as calcic, magnesic, nickelous, cobaltous, plumbic arseniates; for example, in the mineral *pharmacolite*, $\mathbf{As}_2O_5Cao''_2,6\mathbf{O}H_2$ (calcic pyrarseniate), in *nickel ochre*, $\mathbf{As}_2O_5Nio''_3,9\mathbf{O}H_2$, in *cobalt bloom*, $\mathbf{As}_2O_5Coo''_3,8\mathbf{O}H_2$, and in *mimetesite*, $3(\mathbf{As}_2O_5Pbo''_3),\mathbf{Pb}Cl_2$.

Traces of arsenic are almost invariably found in commercial sulphur, iron, copper, tin, and antimony. On account of the solubility of its oxides, arsenic is sometimes found in mineral springs and in the ochreous deposits from mineral waters.

EXAMINATION IN THE DRY WAY.

Arsenic can be completely *volatilized*. When heated in contact with air, either on charcoal or in an open tube, it burns and forms arsenious anhydride, $\mathbf{As}_2O_3$, giving off at the same time a peculiar and most characteristic garlic odour. Arsenical compounds give the same indications when heated by themselves, on charcoal in the reducing flame, and on the addition of sodic carbonate and potassic cyanide, whether the arsenic be present as arsenite or arseniate. The blow-pipe experiments should be performed with great precaution, since arsenical fumes are poisonous. The reaction being so very delicate small quantities only of the substance should be operated upon.

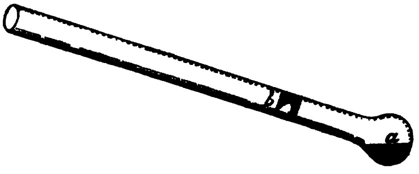


FIG. 77.

When arsenical compounds are heated in a bulb-tube, Fig. 77, *a*, mixed with a proper reducing agent (such as sodic carbonate and charcoal powder), metallic arsenic sublimes and deposits itself in the shape of a lustrous steel grey mirror, *b*, in the upper part of the tube.

EXAMINATION IN THE WET WAY.

Chlorine attacks arsenic violently, forming a highly poisonous liquid, arsenious chloride, $\mathbf{As}Cl_3$. Hydrochloric acid does not act upon arsenic; nitric acid oxidizes it to arsenious and arsenic acids, according to the concentration of the acid.

Arsenic forms *two oxides*, *sulphides*, etc., and *two well characterized series of salts*, *arsenites* and *arseniates* (compare Chapter XVI).

A. **Arsenious compounds.**—We may employ either A SOLUTION OF ARSENIOUS ANHYDRIDE, $\mathbf{As}_2O_3$, in dilute hydrochloric acid, OR AN AQUEOUS SOLUTION OF AN ARSENITE, $\mathbf{As}Ko_3$ (tripotassic arsenite).

$\mathbf{S}H_2$ (**group-reagent**) produces, in an acid solution of $\mathbf{As}_2O_3$ a *lemon yellow* precipitate of **arsenious sulphide**, $\mathbf{As}_2S_3$, readily soluble in caustic alkalies, in alkaline carbonates and sulphides, forming alkaline arsenites and sulpharsenites; it is reprecipitated from any of these solutions, on the addition of dilute hydrochloric or nitric acid. It is nearly insoluble in concentrated hydrochloric acid, even on boiling; but soluble in nitric acid. On digesting freshly precipitated arsenious sulphide in a solution of hydric potassic sulphite, $\mathbf{S}OHoKo$, and excess of sulphurous acid, the yellow precipitate is dissolved, and the solution contains potassic metarsenite, and potassic hyposulphite, after driving off the excess of sulphurous acid by evaporation, thus :—

$$2\mathbf{As}_2S_3 + 16\mathbf{S}OHoKo = 4\mathbf{As}OKo + 6\mathbf{S}SOKo_2 + S_3 + 7\mathbf{S}O_2 + 8\mathbf{O}H_2.$$

$\mathbf{S}Am_2$, same precipitate, soluble in excess.

$\mathbf{N}O_2Ago$ produces from a solution of a neutral arsenite, or from a solution of $\mathbf{As}_2O_3$ in water, rendered neutral by cautiously adding ammonic hydrate, a *yellow* precipitate of **triargentic arsenite**, $\mathbf{As}Ago_3$, readily soluble in ammonic hydrate, ammonic chloride, and nitric acid. The ammoniacal solution of $\mathbf{As}Ago_3$ is decomposed on boiling, with separation of metallic silver and formation of **triargentic arseniate**, $\mathbf{As}OAgo_3$, thus :—

$$\begin{array}{ccccccc} \mathbf{As}Ago_3 & + & \mathbf{O}Ag_2 & = & \mathbf{As}OAgo_3 & + & Ag_2. \\ \text{Soluble in} & & \text{Soluble in} & & \text{Soluble in} & & \text{Black} \\ \text{AmHo.} & & \text{AmHo.} & & \text{AmHo.} & & \text{precipitate.} \end{array}$$

$\mathbf{S}O_2Cuo''$ precipitates a characteristic *yellowish green* precipitate of **hydric cupric arsenite**, $\mathbf{As}HoCuo''$ (*Scheele's green*), from a solution of tripotassic arsenite, readily soluble in ammonic hydrate, ammonic chloride, or nitric acid.

$\mathbf{S}O_2Mgo''$ gives no precipitate in the presence of free ammonic hydrate and ammonic chloride.

Reinsch's test.—Arsenic is precipitated on a strip of clean metallic copper, immersed in a hydrochloric acid solution of $\mathbf{As}_2O_3$, in the form of a grey film of $\mathbf{As}_2Cu_5$, from highly dilute solutions, especially on heating. The film peels off in black scales if the solution contain sufficient arsenic. The presence of the metal should be confirmed in the dry way, especially as antimony is also precipitated by metallic copper under similar conditions.

Arsenious compounds exert a powerful *reducing action*, when brought together with bodies that are capable of parting with oxygen, chlorine, etc. This property is even more marked in arsenious than in antimonious compounds. Triad arsenic compounds, containing two unsatisfied bonds, give rise to numerous interesting reactions, thus :—

$\mathbf{Au}Cl_3$ **(auric chloride)** produces from an acid solution of $\mathbf{As}_2O_3$ a precipitate of metallic gold, and the reaction is so accurate that the amount of arsenic can be determined quantitatively from the weight of the precipitated gold.

Two atoms of Au (2 × 196·7) = three atoms of As (3 × 75).

$$4\mathbf{Au}Cl_3 + 3\mathbf{As}_2O_3 + 6\mathbf{O}H_2 = 3\dot{\mathbf{As}}_2O_5 + Au_4 + 12HCl.$$

Chlorine water, or compounds capable of yielding chlorine, such as a solution of bleaching powder, or of sodic hypochlorite, ClNao (*Eau de Javelle*), oxidize $\mathbf{As}_2O_3$ rapidly, thus :—

$$\mathbf{As}_2O_3 + 2Cl_2 + 2\mathbf{O}H_2 = \mathbf{As}_2O_5 + 4HCl.$$

Iodine, dissolved in a solution of potassic iodide, likewise converts a solution of As_2O_3, dissolved in excess of hydric sodic carbonate, into As_2O_5, with formation of an alkaline iodide, thus:—

$$AsHoNao_2 + 2COHoNao + I_2 = AsOHoNao_2 + 2NaI + OH_2 + 2CO_2.$$

Chlorine, iodine, and bromine act as *oxidizing* agents by decomposing water or a metallic oxide. They form, with the hydrogen or the metal, HCl, HI, HBr, or a corresponding haloid salt, and the oxygen is transferred to the As_2O_3.

The oxidizing action of OAg_2 upon $AsAgo_3$ in an ammoniacal solution has already been noticed.

An analogous change is produced by cupric oxide in the presence of potassic hydrate. On adding to a strongly alkaline solution of tripotassic arsenite a few drops of cupric sulphate, and applying a gentle heat, the blue solution deposits a red precipitate of cuprous oxide, Cu_2O, and leaves tripotassic arseniate, $AsOKo_3$, in solution. (DISTINCTION BETWEEN As_2O_3 AND As_2O_5.)

The deoxidizing action which arsenious compounds exert upon the higher oxides of chromium (chromates) and manganese (manganates and permanganates), has already been described, pages 159 and 173.

B. **Arsenic Compounds.**—We employ AN AQUEOUS SOLUTION OF TRIPOTASSIC ARSENIATE, $AsOKo_3$.

SH_2 gives scarcely any precipitate from an acidulated solution of $AsOKo_3$, until the solution is heated, and a current of gas passed through for some time. It is difficult to effect complete precipitation even then. The precipitate consists of arsenious sulphide and sulphur. It is preferable to reduce the As_2O_5 first to As_2O_3, by a more powerful reducing agent than SH_2, for example, by sulphurous acid, or an acid sulphite, such as $SOHoKo$—

$$AsOKo_3 + SOHo_2 = AsKo_3 + SO_2Ho_2.$$

whence sulphuretted hydrogen precipitates the arsenic readily as arsenious sulphide.

NO_2Ago gives a *reddish brown* precipitate of **triargentic arseniate**, $AsOAgo_3$, soluble in ammonic hydrate and in nitric acid.

SO_2CuO'' produces a *pale greenish blue* precipitate of **hydric cupric arseniate**, $AsOHoCuo''$, soluble in ammonic hydrate and nitric acid.

SO_2Mgo'', in the presence of ammonic chloride and ammonic hydrate, gives a *white crystalline* precipitate of **ammonic magnesic arseniate**, $AsOAmoMgo''$ (DISTINCTION OF As_2O_3 FROM As_2O_5).

Fe_2Cl_6 gives a *yellowish white* precipitate of **ferric arseniate**, $As_2O_2Fe_2o^{vi}$.

$\left(\left\{\begin{matrix}CH_3\\CO\end{matrix}\right.\right)_2Pbo''$ (**plumbic acetate**) gives a *white* precipitate of **triplumbic arseniate**, $As_2O_2Pbo''_3$.

MO_2Amo_2 (**ammonic molybdate**), dissolved in nitric acid, gives a *yellow* precipitate of **arsenio-ammonic molybdate.**

Metallic copper does not precipitate metallic arsenic from dilute acid solutions of As_2O_5; but on adding concentrated hydrochloric acid, and heating, a grey film of As_2Cu_5 is obtained (DISTINCTION BETWEEN As_2O_3 AND As_2O_5).

Arsenious as well as arsenic compounds are capable of oxidizing other bodies, and become themselves reduced either to a lower oxide, sulphide, or to the metallic state.

$\mathbf{S}O_2$ reduces arsenic to arsenious acid.

$\mathbf{S}SONao_2$ (**sodic hyposulphite**) deprives $\mathbf{As}_2O_3$ of its oxygen, and converts it into $\mathbf{As}_2S_3$, thus:—

$$\mathbf{As}_2O_3 + 3\mathbf{S}SONao_2 = \mathbf{As}_2S_3 + 3\mathbf{S}O_2Nao_2.$$

Carbon reduces both Oxides of Arsenic to Metallic Arsenic.—A fragment of the solid arsenical compound is placed in the pointed end, *a*, of a hard glass tube drawn out before the blowpipe, as seen in Fig. 78. A piece of well ignited charcoal is next placed in the narrow part of the tube, at *b*, somewhat above the fragment of the arsenical compound. This charcoal is heated over a gas flame or the flame of a spirit-lamp. When the charcoal is well ignited a second flame is applied to the lower end of the tube in order to volatilize the arsenical compound. The vapour on passing over the glowing charcoal is deprived of its oxygen, and metallic arsenic is deposited in the form of a shining black mirror on the inside of the tube, above the charcoal, at *c*. The reaction takes place according to the equation:—

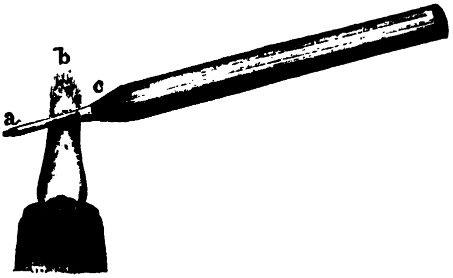


FIG. 78.

$$2\mathbf{As}_2O_3 + 3C = \mathbf{As}_4 + 3\mathbf{C}O_2.$$

This test is very delicate. Arsenic, in the form of an arsenite or arseniate, is liberated by mixing perfectly dry charcoal powder or black flux with the dry substance, previous to its introduction into the drawn out portion of the tube, which for this purpose has a small bulb blown at its lower end. The sublimation of metallic arsenic is accompanied by the characteristic *garlic odour*.

KCy reduces arsenical compounds—oxides as well as sulphides—with formation of potassic cyanate or sulphocyanate. A mixture of potassic cyanide with the arsenical compound is heated in a bulb tube *a* (Fig. 79). Metallic arsenic is deposited at *b*.

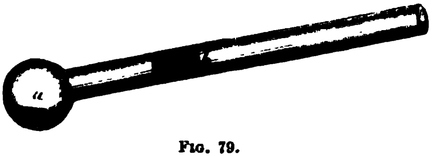


FIG. 79.

The changes are expressed as follows:—

$$2\mathbf{As}_2O_3 + 6KCy = \underset{\substack{\text{Potassic}\\\text{cyanate.}}}{6CyKo} + As_4.$$

$$2\mathbf{As}_2S_3 + 6KCy = \underset{\substack{\text{Potassic}\\\text{sulphocyanate.}}}{6CyKs} + As_4.$$

But since potassic cyanide contains potassic cyanate, as well as potassic carbonate (its composition may be expressed by the formula $5KCy + CyKo + x\mathbf{C}OKo_2$), a *portion* only of the arsenic in $\mathbf{As}_2S_3$ is obtained in the metallic form, and a sulpharseniate is formed which is not reduced by potassic cyanide. On mixing the arsenious sulphide with sulphur, the whole of the arsenic remains behind in the fused mass, as sulpharseniate, and no metallic deposit is obtained. (In the presence of sulphides of Pb, Cu, Ag, Au, Ni, Co, Fe—as, *e.g.*, of $\mathbf{Fe}S_2$ in *arsenical pyrites*, $\mathbf{Ni}S_2$, in *nickel glance*—which are reduced to the metallic state by the action of potassic cyanide, scarcely any arsenical mirror is obtained, because the liberated metallic arsenic—a portion only of the arsenic being liberated—would immediately alloy itself with the metals). These changes are expressed by the equations:—

$$(1)\ 5\mathbf{As}_2S_3 = 3\mathbf{As}_2S_5 + As_4.$$
$$(2)\ 4\mathbf{As}_2S_5 + 12\mathbf{C}OKo_2 = 5\mathbf{As}SKs_3 + 3\mathbf{As}OKo_3 + 12\mathbf{C}O_2.$$

The reduction is generally effected by mixing dry arsenious sulphide with one part of potassic cyanide and three parts of sodic carbonate, and introducing the mixture into a piece of combustion tube, C, drawn out to a point, as seen on a larger scale in Fig. 80. A slow current of carbonic anhydride generated from

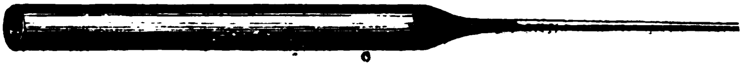


FIG. 80.

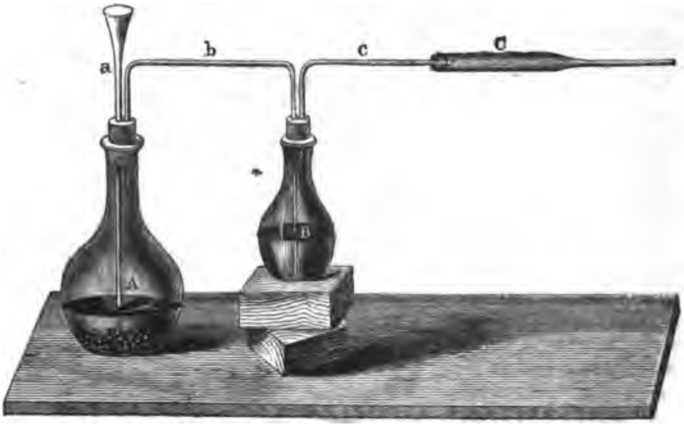


FIG. 81.

marble and hydrochloric acid in the flask A, Fig. 81, and dried by passing through *b* into the flask B, containing concentrated sulphuric acid, and out through the delivery tube *e*, is passed over the mixture in the tube *C*, heated at first gently, till all the moisture has been driven out, and then strongly to fusion, —when a mirror of metallic arsenic collects in the neck of the drawn-out tube.

The reaction has this advantage that no antimony mirror is obtained in the same way.

In order, however, to avoid missing the arsenic, either altogether or obtaining only a portion of it, as stated above, it is preferable to treat the arsenious sulphide with a few drops of concentrated nitric acid, and to evaporate with a little sulphuric acid (in order to decompose any metallic nitrates, if present). The sulphuric acid is next neutralised with sodic carbonate and the mass thoroughly dried, before mixing it with potassic cyanide and reducing it as described. The fused mass retains the antimony, and a good arsenical mirror is obtained, provided no lead, copper, or other reducible metals were present.

$\mathbf{As}_2O_3$ and $\mathbf{As}_2O_5$ are reduced by nascent hydrogen which combines with the oxygen of the arsenical oxides to form water, whilst the arsenic in its nascent state, or the very moment it is liberated from the oxygen, combines likewise with hydrogen to form a gaseous compound of arsenic, called *arseniетted hydrogen* (arsenious hydride) —$\mathbf{As}'''H_3$. This gas is obtained pure by acting with dilute sulphuric acid upon an alloy of zinc and arsenic. The zinc takes the place of the hydrogen in the acid, and arseniated hydrogen is liberated, thus:—

$$\mathbf{As}_2Zn_3 + 3\mathbf{S}O_2Ho_2 = 3\mathbf{S}O_2Zno'' + 2\mathbf{As}H_3.$$

Arseniетted hydrogen is an exceedingly poisonous gas, and the student should on no account attempt to prepare it pure. Its properties may be studied equally well in a mixture of the gas with much hydrogen.

The experiment should be conducted in a closet, connected with a chimney or flue, where a good indraught of air can be obtained. Arseniетted hydrogen possesses a very nauseous odour, and burns with a peculiarly livid bluish flame, when the jet of hydrogen and arseniетted hydrogen gas is lighted, owing to the combustion of arsenic to arsenious anhydride which rises in white fumes.

Generate hydrogen in a flask, *a*, Fig. 82, from pure zinc (free from arsenic) and pure dilute sulphuric acid. Dry the gas by passing it over calcic chloride and connect the drying tube, *b*, with a piece of hard glass tubing, *c*, drawn out

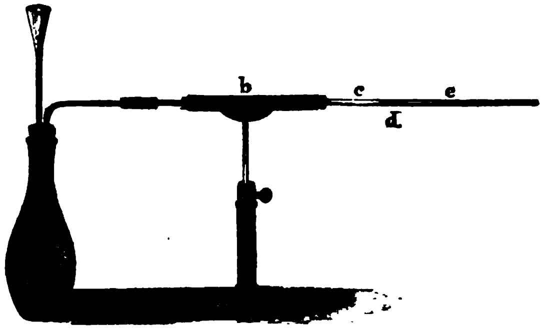


FIG. 82.

to a jet. The hydrogen gas may be ignited at the jet, *as soon as it has displaced the air in the generating flask, a, and drying tube, b.* It burns with an almost colourless flame, if the zinc and acid are pure. On introducing a few drops of an arsenious or arsenic solution through the funnel-tube, the flame is seen to change to blue, and on depressing a piece of porcelain (*e.g.*, a dish, or porcelain crucible) into the flame, a black mirror or deposit of metallic arsenic is obtained. Or the metal may be collected — by heating the glass tube through which the arsenietted hydrogen passes—in the form of a metallic ring, *d*, which deposits within the tube immediately behind the spot where the glass is heated. The hydrogen should not be generated too rapidly, if a good ring is to be obtained. The mirror may be driven on to *e* by gradually moving the flame from *c* towards *d*.

Several arsenical mirrors may be obtained, if a long piece of combustion tube, Fig. 83, be employed, which has been narrowed in several places by drawing it out in the flame of a blowpipe. Arsenietted hydrogen is generated in the flask, *a*, and passing through *b*, the drying tube, *c*, and combustion tube, *d*, issues from the drawn-out jet, where it can be burnt. The tube, *d*, is heated in one or in several places, just before the several drawn-out narrow parts. An arsenical mirror is obtained a little behind the heated part of the tube, as seen in Fig. 83. Little or no arsenietted hydrogen need thus escape from the jet, especially if a slow current of hydrogen be generated.

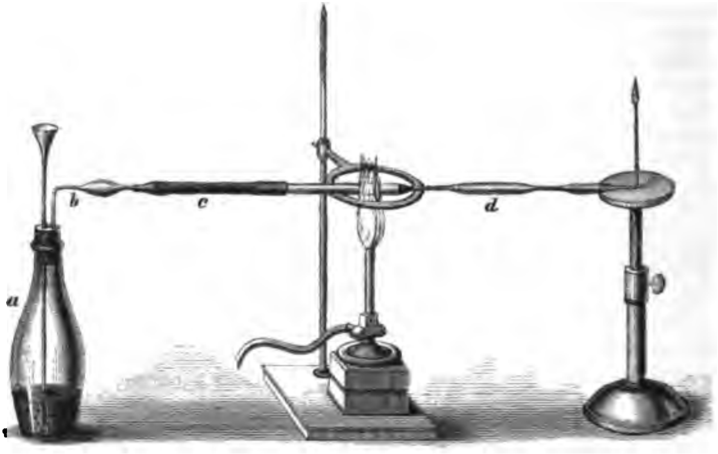


FIG. 83.

The deposition of arsenic in the tube or on the cold porcelain arises from the decomposition of the arsenietted hydrogen, which, at a high temperature, is broken up into arsenic which is deposited, and hydrogen which passes on and burns at the jet. The decomposition which takes place when a cold piece of porcelain is lowered into the flame, is readily explained, if we remember what takes place, when an iron spoon is held in a candle or gas flame. We obtain a deposit of soot (finely-divided carbon from the hydrocarbons), because the combustion is disturbed, and the temperature of the flame suddenly lowered. The flame can only burn, where it is in contact with air, *i.e.*, on the outside. The arsenietted hydrogen on passing through the inner portion of the flame, is decomposed by the heat into arsenic vapour and hydrogen gas; the latter escapes through the outer portion of the flame and is burnt, arsenic being deposited on the cold porcelain surface. The decomposition of arsenietted hydrogen takes place, even if very little of the gas be mixed with much hydrogen gas, and *this test*—known as *Marsh's test* —*is therefore extremely delicate.*

It is of paramount importance that both zinc and sulphuric acid should be tested first. This is done by generating hydrogen, and allowing the gas to escape by itself for some time through the combustion tube ignited in several places.

Care should also be taken to avoid introducing nitric acid, since arsenietted hydrogen is readily decomposed by this acid. It is therefore preferable to dissolve arsenical compounds in hydrochloric acid, with the addition of a few small crystals of potassic chlorate, and to heat gently till no more chlorous odour is observable.

The metal antimony forms with nascent hydrogen a combustible gas analogous to arsenietted hydrogen, called *antimonietted hydrogen* (antimonious hydride), $\mathbf{Sb}H_3$. It is prepared by acting with dilute sulphuric or hydrochloric acid upon an alloy of three atoms of zinc and two atoms of antimony, thus:—

$$\mathbf{Sb}_2Zn_3 + 3\mathbf{S}O_2Ho_2 = 3\mathbf{S}O_2Zno'' + 2\mathbf{Sb}H_3.$$

Mixed with hydrogen gas it is obtained by introducing into a hydrogen apparatus a few drops of an antimony solution ($\mathbf{Sb}Cl_3$, $\mathbf{Sb}O_2Ko$, or tartar emetic). The hydrogen flame turns at once bluish green, and white fumes of antimonious oxide, $\mathbf{Sb}_2O_3$, ascend into the air. The gas has no odour and is not poisonous. On depressing a cold piece of porcelain into the flame, metallic antimony is deposited, and on heating the combustion tube, as in the case of the arsenic experiment, the gas is likewise decomposed into metallic antimony, which collects in the narrowed portions of the tube and forms a *dull black mirror*, and hydrogen, which escapes and can be burnt at the jet.

Since the metallic mirror may consist either of arsenic or antimony, or of a mixture of the two metals (in which case, however, the more volatile arsenic is deposited further away from the flame, and a part of the antimony is found anterior to the spot where the glass tube is heated), it is obvious that we must make further experiments in order to *distinguish* the *arsenic* from the *antimony in the mirror.*

This can be done very readily—

1st. By adding to the mirror obtained on cold porcelain a concentrated solution of bleaching powder, or of sodic hypochlorite (*eau de Javelle*); or by simply exposing the mirror to chlorine gas, evolved by treating a little bleaching powder with dilute hydrochloric acid: the arsenical mirror is dissolved, antimony is not affected, thus:—

$$As_2 + 5ClNao = \mathbf{As}_2O_5 + 5NaCl.$$

2nd. By passing a very slow current of dry sulphuretted hydrogen through the glass tube, containing the arsenic and antimony mirror, and applying a gentle heat. The metals are converted into sulphides—arsenic into lemon-yellow arsenious sulphide, and antimony into a black or partly orange-red antimonious sulphide; and, if both metals are present, the two sulphides appear side by side: the former somewhat in front of the latter, $\mathbf{As}_2\mathrm{S}_3$ being the more volatile of the two sulphides. On passing next a current of dry hydrochloric acid gas without the application of heat, antimonious sulphide disappears entirely, being converted into antimonious chloride, $\mathbf{Sb}\mathrm{Cl}_3$, which volatilizes in the current of hydrochloric acid gas, and may be passed into water and tested by means of sulphuretted hydrogen. Arsenious sulphide remains unaffected, even if the hydrochloric acid gas be passed over it for some time. The residuary $\mathbf{As}_2\mathrm{S}_3$ *dissolves readily in hydric ammonic carbonate*, $\mathbf{C}\mathrm{OHoAmo}$.

Nascent hydrogen, generated by the action of a strong solution of potassic hydrate upon metallic zinc or aluminium, combines with arsenic to form $\mathbf{As}\mathrm{H}_3$, but not with antimony; and the presence of arsenic may be readily recognized in a compound by allowing a jet of the gas to impinge against filter paper dipped in a solution of argentic nitrate, when a bluish black colouration, ($\mathbf{As}\mathrm{Ag}_3$), is produced even by small quantities of arseniretted hydrogen. (DISTINCTION BETWEEN As AND Sb).

$\mathbf{Sb}\mathrm{H}_3$ and $\mathbf{As}\mathrm{H}_3$ can moreover be distinguished from each other by passing a slow current of the mixed gases into a solution of argentic nitrate; argentic oxide, acting the part of an oxidizing agent, converts $\mathbf{As}\mathrm{H}_3$ into $\mathbf{As}_2\mathrm{O}_3$, thus:—

$$\mathbf{As}\mathrm{H}_3 + 6\mathbf{N}\mathrm{O}_2\mathrm{Ago} + 3\mathbf{O}\mathrm{H}_2 = \mathrm{Ag}_6 + \mathbf{As}\mathrm{Ho}_3 + 6\mathbf{N}\mathrm{O}_2\mathrm{Ho}.$$

$\mathbf{Sb}\mathrm{H}_3$ is not acted upon in like manner. The oxidation extends only to the hydrogen of the $\mathbf{Sb}\mathrm{H}_3$, the metallic silver taking the place of the hydrogen, thus:—

$$\mathbf{Sb}\mathrm{H}_3 + 3\mathbf{N}\mathrm{O}_2\mathrm{Ago} = \mathbf{Sb}\mathrm{Ag}_3 + 3\mathbf{N}\mathrm{O}_2\mathrm{Ho}.$$

The arsenious acid is separated by filtration from the $\mathbf{Sb}\mathrm{Ag}_3$ and Ag. On cautiously adding to the filtrate a dilute solution of ammonic hydrate, a *yellow* precipitate of **triargentic arsenite** is obtained where the two layers of the ammonic hydrate and acid solution meet.

The residue consisting of $\mathbf{Sb}\mathrm{Ag}_3$ and Ag is boiled with a solution of tartaric acid, when the antimonious argentide is acted upon with formation of soluble antimonious tartrate (?) silver being left behind. Filter; acidulate the filtrate with dilute hydrochloric acid, and pass $\mathbf{S}\mathrm{H}_2$. An *orange* precipitate indicates antimony.

QUESTIONS AND EXERCISES.

1. Which are the most important natural compounds of arsenic?
2. Translate into graphic formulæ the symbolic formulæ of *realgar*, *orpiment*, *copper nickel*, *smaltine*, *nickel ochre*.
3. Give evidences of the triad and pentad nature of arsenic.
4. What changes does arsenic undergo when heated, 1st, by itself, in a current of a neutral gas ($\mathbf{C}\mathrm{O}_2$ or H); 2ndly, in contact with air; 3rdly, in contact with chlorine?
5. How is metallic arsenic obtained from white arsenic?
6. How can arsenious compounds be distinguished in the presence of arsenic compounds? Give several methods.
7. What action has $\mathbf{S}\mathrm{H}_2$ upon an acid solution of $\mathbf{As}\mathrm{Ho}_3$, and upon a solution of $\mathbf{As}\mathrm{OHo}_3$?
8. Express by an equation the reaction which takes place when $\mathbf{As}_2\mathrm{S}_3$ is dissolved; 1st, in NaHo; 2ndly, in $\mathbf{S}\mathrm{Am}_2$; 3rdly, in $\mathbf{C}\mathrm{OHoAmo}$.
9. What precipitates are produced when argentic nitrate is added to a neutral solution of an arsenite, or arseniate?
10. Why is $\mathbf{As}\mathrm{Ago}_3$, in an ammoniacal solution, converted on boiling into $\mathbf{As}\mathrm{OAgo}_3$? Express the change by equations.
11. What is the action of $\mathbf{S}\mathrm{O}_2\mathrm{Mgo}''$, in an ammoniacal solution, upon arsenious and arsenic solutions?

12. Give a few instances of the reducing action of arsenious compounds. Express the changes by equations.
13. Explain the oxidizing action of Cl, Br, and I upon arsenious compounds.
14. What takes place when metallic copper is introduced into a dilute hydrochloric acid solution: 1st, of $\mathbf{As}_2O_3$; 2ndly, of $\mathbf{As}_2O_5$ (Reinsch's test)?
15. Explain under what conditions arsenic, as well as arsenious compounds act as oxidizing agents. Give examples, and express the changes by equations.
16. Explain why a portion of the arsenic only is liberated, when an arsenical sulphide is heated with potassic cyanide. Give equations.
17. Explain how the presence of free sulphur, or the presence of certain metallic sulphides influences the reduction of arsenical compounds by potassic cyanide. Give equations.
18. Explain the reduction of arsenical compounds by nascent hydrogen (Marsh's test), and show by equations the formation of $\mathbf{As}H_3$.
19. What change does $\mathbf{As}H_3$ undergo: 1st, when burnt in the air; 2ndly, when passed through a tube heated in one or more places; 3rdly, when passed into a solution of argentic nitrate; 4thly, when passed through concentrated nitric acid?
20. Explain the formation of $\mathbf{Sb}H_3$ and state—1st, what properties $\mathbf{As}H_3$ has in common with $\mathbf{Sb}H_3$; and, 2ndly, how it differs from the latter in its chemical deportment with argentic nitrate.
21. How would you distinguish between an arsenic and antimony mirror?
22. State how arsenic can be separated—1st, from antimony, 2ndly, from tin.
23. 1·2 grm. of finely divided gold has been obtained by boiling a solution of arsenious acid with $\mathbf{Au}Cl_3$: how much $\mathbf{As}_2O_3$ by weight did the solution contain?
24. Calculate the percentage composition of ammonic magnesic arseniate, dried at 100° C. ($\mathbf{As}OAmoMgo'' + Aq.$).
25. How much $\mathbf{Sb}H_3$ gas by volume (at 0°C and 760 mm.), and by weight can be obtained by the action of dilute hydrochloric acid upon ·5 grm. of the alloy $\mathbf{Sb}_2Zn_3$?

4. **GOLD**, Au' and $'''$.—Gold is generally found native and is then readily recognized by its colour, malleability, and physical character generally. Gold occurs in anything like considerable quantities in combination only with the rare element tellurium. In small quantities it occasionally accompanies metallic sulphides.

EXAMINATION IN THE DRY WAY.

When heated on charcoal with sodic carbonate and borax in the reducing flame, gold compounds yield a yellow, very malleable globule of metallic gold.

To detect gold in argentiferous minerals in which it is present only in minute quantities, and associated with large quantities of other non-volatile metals, the powdered mineral is fused with borax and metallic lead, and the metallic button cupelled, as will be described under silver. The globule of white metal which is left on the cupel is beaten out, and the silver dissolved by digesting with a little nitric acid in a small porcelain dish. The argentic nitrate is poured off, and the gold washed with distilled water. The black insoluble residue is once more fused on charcoal before the blowpipe, when it assumes the well-known appearance of fine gold.

Old silver coins frequently contain a small quantity of gold, which, on dissolving in nitric acid, is left as a black powder.

When an insufficient quantity of silver is present in the button (which may be inferred from its pale yellow colour), from two to four times its own weight of silver should be fused up with it, and the button so obtained beaten out and then treated with nitric acid in order to separate or "*part*" the gold.—***Method of assaying gold.***

EXAMINATION IN THE WET WAY.

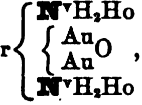
Gold when unalloyed is soluble in *aqua regia* only, forming a SOLUTION OF AURIC CHLORIDE, $\mathbf{Au}Cl_3$, which may be employed for studying the reactions in the wet way.

$\mathbf{S}H_2$ (**group-reagent**) gives from a cold solution a *black* precipitate of **auric sulphide**, $\mathbf{Au}_2S_3$, from a boiling solution, a *brownish* precipitate of **aurous sulphide**, $\mathbf{Au}_2S=\left(\begin{array}{l}''\mathbf{Au}'\\ ''\mathbf{Au}'\end{array}S''\right)$. These precipitates are insoluble in hydrochloric and nitric acids, but dissolve in aqua regia. They are likewise insoluble in ammonic sulphide, but soluble, although with difficulty, in yellow sulphide, more readily in yellow sodic sulphide, forming a sulpho-salt, $\mathbf{Au}Nas_3$.

$\mathbf{S}Am_2$ and $\mathbf{S}SONao_2$, same precipitate.

KHo or NaHo produces no precipitate.

AmHo produces from a concentrated solution of auric chloride a *reddish yellow* precipitate of **ammonic aurate** or **fulminating gold**, $(\mathbf{N}H_3)_2Au_2O_3$, or



$$\left\{\begin{array}{l}\mathbf{N}^{v}H_2Ho\\ \left\{\begin{array}{l}Au\\ Au\end{array}\right.O\\ \mathbf{N}^{v}H_2Ho\end{array}\right.$$

, thus:—

$$2\mathbf{Au}Cl_3 + 8AmHo = (\mathbf{N}H_3)_2Au_2O_3 + 6AmCl + 5\mathbf{O}H_2.$$

The detection of gold is attended with no difficulty, owing to the facility with which auric chloride is reduced to the metallic state. Gold has little affinity for non-metallic elements; and the compounds which it forms with them are readily broken up by heat alone, or on being brought in contact with bodies which have more affinity for the metalloids, leaving metallic gold in a finely divided condition, as a brown powder, which acquires metallic lustre when dried and rubbed in a mortar. Hence in auric chloride we possess a powerful *oxidizing* agent, as we have already seen under tin, antimony, and arsenic. The same oxidizing action is called into play, when $\mathbf{Au}Cl_3$ comes together with solutions of $\mathbf{S}OHo_2$, oxalic acid, $\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}OHo\end{array}\right.$, $\mathbf{S}O_2Feo''$ or $\mathbf{Fe}''Cl_2$, $\mathbf{Cu}_2Cl_2$, dissolved in hydrochloric acid, $\begin{array}{l}\mathbf{N}O_2\\ \mathbf{N}O_2\end{array}Hg_2o''$, $\mathbf{N}OKo$, sugar in an alkaline liquid, and many other organic substances (*e.g.*, the epidermis); arseniettted, antimonietted, and phosphoretted hydrogen decompose $\mathbf{Au}Cl_3$ likewise.

The following equations express these changes:—

(1) $2\mathbf{Au}Cl_3$, when ignited splits up into $Au_2 + 3Cl_2$.
(2) $\mathbf{Au}_2S_3$, " " " $Au_2 + S_3$.

$$\begin{array}{llll}
(3)\ 2\mathbf{Au}Cl_3 + 3\mathbf{S}OHo_2 + 3\mathbf{O}H_2 & = Au_2 + 3\mathbf{S}O_2Ho_2 & + 6HCl. & \\
(4)\ 2\mathbf{Au}Cl_3 + 3\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right. & = Au_2 + 6\mathbf{C}O_2 & + 6HCl. & \\
(5)\ 2\mathbf{Au}Cl_3 + 6\mathbf{Fe}Cl_2 & = Au_2 + 3\mathbf{Fe}_2Cl_6. & & \\
(6)\ 2\mathbf{Au}Cl_3 + 6\mathbf{S}O_2Feo'' & = Au_2 + \mathbf{Fe}_2Cl_6 & + & 2\mathbf{S}_3O_6Fe_2o^{vi}. \\
(7)\ 2\mathbf{Au}Cl_3 + 3\mathbf{Cu}_2Cl_2 & = Au_2 + 6\mathbf{Cu}Cl_2. & & \\
(8)\ 2\mathbf{Au}Cl_3 + 3\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Hg_2o'' & = Au_2 + 3\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Hgo'' & + 3\mathbf{Hg}Cl_2. & \\
(9)\ 2\mathbf{Au}Cl_3 + 3\mathbf{N}OKo + 3\mathbf{O}H_2 & = Au_2 + 3\mathbf{N}O_2Ko & + 6HCl. & \\
(10)\ 2\mathbf{Au}Cl_3 + 2\mathbf{As}H_3 + 3\mathbf{O}H_2 & = Au_2 + 2\mathbf{As}Ho_3 & + 6HCl. & \\
(11)\ 2\mathbf{Au}Cl_3 + \mathbf{Sb}H_3 & = Au_2 + \mathbf{Sb}Cl_3 & + 3HCl. &
\end{array}$$

In the analysis of a solution containing gold, as well as some other metals of Group II precipitable by $\mathbf{S}H_2$, it is usual to first remove the gold in the metallic state, by boiling with oxalic and hydrochloric acids, before passing $\mathbf{S}H_2$. The precipitated gold is collected on a filter and fused to a button on charcoal.

Gold is precipitated from a hydrochloric acid solution of $\mathbf{Au}Cl_3$ by most metals, even by Pt, Ag, and Hg.

QUESTIONS AND EXERCISES.

1. How would you treat a silver coin containing a small quantity of gold, in order to extract this latter metal from it?
2. How is $\mathbf{Au}Cl_3$ prepared?
3. Translate into graphic formulæ the following constitutional formulæ, $\mathbf{Au}Cl_3$, $\left\{\begin{matrix}\mathbf{Au}O\\ O\\ \mathbf{Au}O\end{matrix}\right.$, $\left\{\begin{matrix}\mathbf{Au}S\\ S\\ \mathbf{Au}S\end{matrix}\right.$, $\begin{matrix}''\mathbf{Au}'\\ ''\mathbf{Au}'\end{matrix}S$.
4. Describe how pure metallic gold is prepared from $\mathbf{Au}Cl_3$, in the wet way.
5. Explain the change which $\mathbf{Au}_2S_3$ undergoes, 1st, when gently heated in a bulb tube; 2nd, when heated in a tube open at both ends.
6. What reaction takes place when $\mathbf{Au}Cl_3$ is brought together with bodies which have any latent bonds left? Give instances of such reactions and express the changes by equations.
7. How can gold be separated from an alloy of Au, Ag, and Cu?
8. 9·37 grms. of a gold mineral, when treated with aqua regia and reduced by $\mathbf{Fe}Cl_2$, yield ·53 grm. of metallic Au; what is the percentage of gold in the mineral?
9. How much chlorine gas, by weight and by volume, can be obtained by the ignition of 1·25 grm. of $\mathbf{Au}Cl_3$?
10. What action takes place when a piece of gold is suspended from the positive electrode in a bath of $\mathbf{Au}Cl_3$, metallic copper forming the negative electrode? Explain the process of electro-gilding.

5. **PLATINUM**, Pt'' and ^{iv}.—This metal is found native, but more frequently alloyed with other metals. It is characterized by its infusibility before the blowpipe, and is not acted upon by the usual fluxes. It can, therefore, only be examined *in the wet way.*

Unalloyed platinum is not attacked by either nitric, hydrochloric, or sulphuric acid, but by *aqua regia* (comp. page 87), with formation of platinic chloride, $\mathbf{Pt}Cl_4$. A SOLUTION OF THIS SALT is employed for studying the reactions of platinum.

$\mathbf{S}H_2$ **(group-reagent)** produces slowly a *dark brown* precipitate of **platinic disulphide**, $\mathbf{Pt}S_2$. On heating, the precipitate forms quickly. It is insoluble in nitric or hydrochloric acid, soluble in aqua regia; difficultly soluble in normal ammonic sulphide, more speedily in yellow sulphide, with which it forms a sulpho-salt, $\mathbf{Pt}SAm_2$. Heated out of contact with air, it is decomposed into $\mathbf{Pt}''S$ and $\mathbf{S}$.

$\mathbf{S}Am_2$, same precipitate.

$\mathbf{Pt}Cl_4$ is interesting on account of the compounds which it forms with the chlorides of the alkali metals (and with the chlorides of many organic bodies, *e.g.*, the so-called alkaloids, such as quinine, nicotine, etc.).

AmCl produces a *light yellow crystalline* precipitate of **ammonic platinic chloride**, $2AmCl,\mathbf{Pt}Cl_4$. From dilute solutions a precipitate is obtained only after evaporation on a water-bath. The precipitate is somewhat soluble in water, insoluble in alcohol.

KCl produces a *yellow crystalline* precipitate of **potassic platinic chloride**, $2KCl,\mathbf{Pt}Cl_4$, analogous in its appearance and properties to the precipitate just described.

NaCl forms with platinic chloride a double chloride, which is, however, soluble in water, and is obtained in needle-shaped crystals only after considerable evaporation.

The precipitate produced by platinic chloride with AmCl and KCl serves for the detection and isolation of platinum, and *vice versâ*, for the detection of ammonium or potassium compounds. (Comp. Chapter II, Part II.)

Platinum is capable of forming a lower chloride, viz., platinous chloride, $\mathbf{Pt}''Cl_2$, in which the platinum acts as a dyad. This salt is obtained by heating the platinic chloride for some time in an air- or oil-bath up to 204° C., as long as any chlorine is evolved; or by acting with sulphurous acid upon a solution of platinic chloride, until the latter ceases to give a precipitate with ammonic chloride. $\mathbf{Pt}Cl_2$ is a greenish grey powder, *insoluble* in water, but soluble in hydrochloric acid.

Several reactions in the wet way for platinum are based upon the power, which its salts possess, of oxidizing other bodies which have some bonds left unsatisfied; but as platinic salts are not so easily reduced as gold salts, a solution of the latter metal is generally preferred. After what has been stated under gold, the following reactions will be readily understood:—

$\mathbf{Pt}Cl_4$ produces with $\mathbf{Sn}Cl_2$ only a dark brownish red colour, owing to the reduction of the platinic to platinous chloride.

$\mathbf{Pt}Cl_4$ is reduced by $\mathbf{S}O_2Feo''$ only after long continued boiling.

$\mathbf{Pt}Cl_4$ is reduced to platinum by formic acid $\left\{\begin{matrix}H\\ \mathbf{C}OHo\end{matrix}\right.$, on heating, if the free acid be neutralized with sodic carbonate.

Metallic zinc precipitates metallic platinum.

It is obvious that platinous chloride could act as a reducing agent, but it is rarely employed for this purpose.

Whenever platinum and gold are contained in a solution, together with other metals of Group II, precipitable by $\mathbf{S}H_2$, it is preferable to remove the gold, by means of oxalic acid (which does not reduce platinic chloride), before removing the platinum by evaporation with ammonic chloride.

QUESTIONS AND EXERCISES.

1. How is $\mathbf{Pt}Cl_4$ prepared? Give equation.
2. How much metallic platinum is left when two grms. of $\mathbf{Pt}S_2$ are strongly ignited in a porcelain crucible?
3. How are $2AmCl,\mathbf{Pt}Cl_4$ and $2KCl,\mathbf{Pt}Cl_4$ affected by heat? Express the changes by equations.
4. How much Pt will be left, when 1·5 grm. of $2AmCl,\mathbf{Pt}Cl_4$ are ignited?
5. Calculate how much potassic platinic chloride ought to be obtained from ·521 grm. of KCl.
6. How is $\mathbf{Pt}Cl_2$ prepared?

Separation of the metals arsenic, antimony, and tin, whose sulphides are soluble in yellow ammonic sulphide, or in sodic hydrate.

The precipitate produced by the group-reagent $\mathbf{S}H_2$ is soluble in yellow ammonic sulphide, or in sodic hydrate, and may consist of three sulphides. If the precipitate be of a dark brown colour, it may be inferred that $\mathbf{Sn}S$ is present. If it be of a fine lemon-yellow colour, the presence of arsenious or stannic sulphide may be inferred, if orange-coloured, antimony should be looked for.

The three sulphides are unequally soluble in hydric ammonic carbonate. $\mathbf{As}_2S_3$ dissolves freely, $\mathbf{Sn}S_2$ very slightly, and $\mathbf{Sb}_2S_3$ is insoluble. On digesting, therefore, the precipitate with $\mathbf{C}OHoAmo$, and filtering, arsenic is obtained in the filtrate; and antimony and tin are left in the residue. In order to separate the remaining two metals, the antimony is converted into antimonietted hydrogen, since tin does not form a gaseous compound with hydrogen. For this purpose the two sulphides are dissolved in hot hydrochloric acid, and the solution of the mixed chlorides introduced into a Marsh's apparatus. Antimony is detected by the metallic deposit which $\mathbf{Sb}H_3$ gives on porcelain, insoluble in ClNao. Tin is found in the generating flask as a black powder. The greyish metal is removed from the undissolved zinc, dissolved in hot hydrochloric acid (by the aid of a little platinum foil), and the solution tested with mercuric chloride. A white precipitate of mercurous chloride, $\mathbf{Hg}_2Cl_2$, indicates the presence of tin.

The separation of arsenic, antimony, and tin, may thus be based upon—

1. *The solubility of* $\mathbf{As}_2S_3$ *in hydric ammonic carbonate.*
2. *The formation of antimonietted hydrogen.*
3. *The precipitation of tin by metallic zinc.*

A tabular scheme, embodying this method of separation, will be found in Table II in the Analytical Tables at the end of the book.

Several other methods of recognizing and separating the metals tin, antimony, and arsenic, will readily suggest themselves. The student should draw up tabular schemes, embodying the following five methods.

A method of separation of As, Sb and Sn, may be based upon:—

1st. The oxidation of $\mathbf{As}_2S_3$, $\mathbf{Sb}_2S_3$ and $\mathbf{Sn}S$ by concentrated nitric acid; and the conversion of the three oxides (by fusion with caustic soda in a silver crucible) into sodic metantimoniate, arseniate and stannate.

2nd. The insolubility of $\mathbf{Sb}O_2Nao$ in water and alcohol ($\mathbf{As}ONao_3$ and $\mathbf{Sn}ONao_2$ being soluble).

3rd. The conversion of $\mathbf{As}ONao_3$ and $\mathbf{Sn}ONao_2$ into $\mathbf{As}_2S_3$ and $\mathbf{Sn}S$, by means of sulphurous acid and sulphuretted hydrogen.

4th. The volatility of $\mathbf{As}_2S_3$ when heated in a current of dry $\mathbf{S}H_2$ gas, $\mathbf{Sn}S$ being non-volatile.

5th. The absorption of the volatilized $\mathbf{As}_2S_3$ in a solution of sodic hydrate, oxidation by chlorine and precipitation as $\mathbf{As}OAmoMgo''$.

6th. The conversion of the non-volatile $\mathbf{Sn}S$ into $\mathbf{Sn}O_2$ by ignition in air.

Another method is based upon:—

1st. The precipitation of arsenic and antimony in the form of sulphides, by boiling a hydrochloric acid solution of the three metals with sodic hyposulphite, tin remaining in solution.

2nd. By boiling the precipitated $\mathbf{As}_2S_3$ and $\mathbf{Sb}_2S_3$ with hydric potassic sulphite and sulphurous acid; $\mathbf{As}_2S_3$ is converted into potassic metarsenite, $\mathbf{Sb}_2S_3$ remains undissolved.

A third method consists in:—

1st. Removing the $\mathbf{As}_2S_3$, by boiling with hydric sodic sulphite and sulphurous acid; the other two sulphides are not dissolved.

2nd. The oxidation of the undissolved $\mathbf{Sb}_2S_3$ and $\mathbf{Sn}S_2$ with concentrated nitric acid and boiling with tartaric acid: $\mathbf{Sb}_2O_4$ is soluble, $\mathbf{Sn}O_2$ remains undissolved.

A fourth method of recognizing arsenic, antimony, and tin, is based upon:—

1st. The introduction of a solution (in HCl and KO_3Cl) of the three sulphides into a hydrogen apparatus, and passing the evolved arsenietted and antimoniettėd hydrogen through a solution of argentic nitrate; the tin remains behind precipitated on the zinc.

2nd. The solubility of the precipitated $\mathbf{Sb}Ag_3$ in tartaric acid, and precipitation of the antimony by means of sulphuretted hydrogen from a hydrochloric acid solution.

3rd. The precipitation of the $\mathbf{As}Ago_3$ from the argentic nitrate solution by means of ammonia.

A fifth method of recognizing the metals of Group IIB, depends upon:—

1st. The insolubility of $\mathbf{As}_2S_3$ in strong hydrochloric acid,

$\mathbf{Sb}_2S_3$ and $\mathbf{Sn}S_2$ being dissolved. The presence of arsenic is confirmed by fusion with potassic cyanide and sodic carbonate.

2nd. The precipitation of the antimony on platinum by means of metallic zinc; a black stain indicates antimony.

3rd. Dissolving the tin precipitated on the zinc in hydrochloric acid and confirming its presence by means of mercuric chloride.

PRACTICAL EXERCISES AND QUESTIONS ON GROUP IIB.

1. $\mathbf{S}H_2$ produces a fine yellow precipitate, a portion of which is soluble in ammonic sulphide. What inference would you draw from this, and how would you examine both the solution and the residuary yellow sulphide?
2. Describe several methods for separating As from Sb.
3. Examine some green paper-hangings for As (Scheele's green).
4. Test a sample of commercial hydrochloric acid for As and Fe.
5. Separate As from Sn in a solution of $\mathbf{Sn}Cl_2$ and $\mathbf{As}_2O_3$, containing ·500 grm. of Sn, and ·020 grm. of As.
6. Analyze a solution containing ·010 grm. of As and ·100 grm. of Sb, by converting the two metals into the respective hydrogen compounds.
7. You have given to you a hydrochloric acid solution containing ·200 grm. of Sn and ·020 grm. of Sb; also a strip of zinc and a piece of platinum foil. Describe how you would separate the two metals.
8. Test a sample of *iron pyrites*, $\mathbf{Fe}S_2$, for arsenic, in the dry and in the wet way.
9. A precipitate consists of $\mathbf{Sb}_2S_3$ and $\mathbf{As}_2S_3$. Describe different methods of analysis, and state the possible causes of error inherent upon each method.
10. Analyze a mixture of $\mathbf{Sn}O_2$ and $\mathbf{Sb}_2O_4$, both in the dry and wet way.
11. You have given to you a solution, containing potassic arsenite and arseniate. State how you would identify the two oxides of arsenic in the presence of each other.
12. Test a solution of stannic chloride for stannous chloride.
13. How can you detect traces of antimonic chloride in a solution of antimonious chloride?
14. What are the changes which $\mathbf{As}_2S_3$, $\mathbf{Sb}_2S_3$ and $\mathbf{Sn}S_2$ undergo, when they are treated with concentrated nitric acid and when the products of the oxidation are fused with caustic soda?

CHAPTER VI.

REACTIONS OF THE METALS OF GROUP I.

This group comprises the metals SILVER, LEAD, and MERCURY in the form of mercurous compounds, which are precipitated by dilute hydrochloric acid.

1. **SILVER**, Ag'.—This metal occurs *native;* also as SULPHIDE, in *silver glance*, $\mathbf{S}Ag_2$, and in combination with antimony, as sulpho-salt in trisulphargentic orthosulphantimonite, or *dark red silver ore* (*pyrargyrite*), $\mathbf{Sb}Ags_3$; with arsenic as trisulphargentic sulpharsenite, in *proustite*, $\mathbf{As}Ags_3$; as CHLORIDE, AgCl, in *horn silver*, and other ores.

EXAMINATION IN THE DRY WAY.

Place a small quantity of powdered *silver glance* towards the middle of a hard glass tube (combustion tubing of about ¼ inch internal diameter, cut with a sharp file into lengths of 5 to 6 inches, answers best). Heat the powder gradually by moving the tube about in a Bunsen gas flame, and lastly, heat it strongly towards the centre. By holding the tube in a slightly slanting position, a current of air is made to pass over the ignited sulphide; the sulphur becomes oxidized and is carried off as sulphurous anhydride, readily recognizable by its pungent odour. Metallic silver is left, together with a little argentic sulphate.

Other volatile bodies, such as antimony, arsenic (selenium and tellurium), which are frequently present in pyritical silver ores, are likewise oxidized, but are to a great extent deposited as $\mathbf{As}_2O_3$ and $\mathbf{Sb}_2O_3$, in the cool part of the tube.

Mix a little of the finely-powdered *silver glance* (or of the roasted ore) with sodic carbonate, and heat upon charcoal under the reducing flame of the blowpipe. A globule of bright metallic silver is left, which is, however, almost invariably contaminated with a little carbon.

Silver ores which contain no other fixed element but silver, are reduced on charcoal to the metallic state by a simple fusion with sodic carbonate. Antimony and arsenic, if present, are readily volatilized, as metals, before the reducing flame. The sulphur combines with the alkali metal.

Silver ores which contain non-volatile metals, such as copper, iron, etc., as in *argentiferous fahl ore*, and from which the metal silver could not be eliminated before the blowpipe flame, are treated in the following manner:—

Mix ·100 grm. of the finely-powdered ore with its own bulk of pounded borax glass; wrap it up in a small piece of assay lead;* introduce it into a cavity, made in a good piece of charcoal, and fuse under the reducing flame of the blowpipe, at first gently and afterwards more strongly. The heat is kept up till the whole mass has resolved itself into a metallic button and a clear glassy borax bead, which does not adhere to the charcoal. Should the metallic button, on cooling, present a dull grey surface, indicative of the presence of antimony, it is next heated in the oxidizing flame, until on cooling, it shows a bright, somewhat prismatic surface. It is then detached from the borax, cleaned by a blow with a hammer and carefully cupelled on some bone-ash (tricalcic phosphate, $\mathbf{P}_2O_2Cao''_3$), pressed into a shallow cavity in a piece of charcoal, the surface being made smooth and thoroughly concave with the round end of a pestle. The button is thoroughly freed from borax, placed in the cupel and heated in the oxidizing flame. The lead is oxidized and absorbed by the porous bone-ash, forming a mass of fused litharge around the metallic bead. If one cupellation does not yield a brilliant white globule of silver, *i.e.*, if the copper has not been entirely removed—a fact which is indicated by a black colour, instead of the pale yellow colour of the litharge, in the cupel—the cupellation of the button must be repeated in a fresh cupel, and the button, if necessary, re-melted with a small quantity of assay lead. The silver not being an oxidizable metal, is obtained in the metallic state.

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* Lead free from silver, prepared from plumbic acetate.

Small quantities of silver must be separated from lead (as well as from other metals), *by cupellation.*

Fuse some finely powdered *argentiferous galena*, $\mathbf{Pb}S, \mathbf{S}Ag_2$ (or $\mathbf{Pb}Ags_2$), on charcoal before the reducing flame of the blowpipe, either alone or with sodic carbonate. A bead of an alloy of much lead and very little silver is left. Expose this bead on a small cupel (Fig. 84) to the oxidizing action of the blowpipe flame. The lead is oxidized and absorbed by the cupel, metallic silver being left.

FIG. 84.

Dried AgCl is mixed with dry $\mathbf{C}ONao_2$ in a small mortar, transferred to the charcoal and heated in the reducing flame of the blow-pipe. A button of metallic silver is left, thus:—

$$(1)\ 2AgCl + \mathbf{C}ONao_2 = 2NaCl + \mathbf{C}O_2 + O + Ag_2.$$

REACTIONS IN THE WET WAY.

For the reactions of silver in the wet way we employ A SOLUTION OF ARGENTIC NITRATE, $\mathbf{N}O_2Ago$.

HCl (**group-reagent**), and **soluble chlorides** (NaCl, etc.) give a *white curdy* precipitate of **argentic chloride**, AgCl, which turns *violet* on exposure to light. The precipitate is insoluble in water and dilute acids; slightly soluble in concentrated nitric and hydrochloric acids; readily soluble in ammonic hydrate, potassic cyanide, and sodic hyposulphite; soluble also to a perceptible extent in concentrated hydrochloric acid and in saturated solutions of alkaline chlorides, more particularly when heated, whence the dissolved argentic chloride is, however, reprecipitated on dilution with water.

Collect the precipitated AgCl on a filter and dry over a sand-bath (see Fig. 69). Fuse a portion of the dried AgCl in a porcelain crucible over a small gas flame. The white powder fuses; it undergoes a mere physical change, and leaves on cooling a hard mass, called *horn silver*.

Place a small piece of zinc on the fused *horn silver*, and add a drop of dilute hydrochloric acid and a little water. A voltaic action is set up between the metallic zinc and silver. The zinc removes the chlorine and leaves the metallic silver. The same action takes place when the white curdy precipitate of argentic chloride is brought in contact with strips of metallic zinc.

This forms a convenient method of recovering silver from silver residues.

NaHo or KHo precipitates **argentic oxide**, $\mathbf{O}Ag_2$, in the form of a *brown powder*, which, on strong ignition, gives off oxygen and is converted into metallic silver.

AmHo, when gradually added, precipitates argentic oxide, readily soluble in excess.

$\mathbf{S}H_2$ precipitates *black* **argentic sulphide**, $\mathbf{S}Ag_2$, from acid solutions; insoluble in dilute acids, in alkalies, alkaline sulphides, and potassic cyanide; readily soluble in dilute boiling nitric acid with separation of sulphur.

$\mathbf{S}Am_2$ (or any **soluble sulphide**) precipitates from neutral solutions *black* **argentic sulphide.**

HI or KI gives a *yellowish* precipitate of **argentic iodide**, AgI, insoluble in dilute nitric acid; almost insoluble in ammonic hydrate (DISTINCTION BETWEEN AgCl AND AgBr).

HBr or KBr gives a *yellowish white curdy* precipitate of **argentic bromide**, AgBr; insoluble in dilute nitric acid; difficultly soluble in ammonic hydrate; readily soluble in potassic cyanide or sodic hyposulphite, decomposed by concentrated hydrochloric acid, with evolution of bromine vapour and conversion into AgCl.

HCy or KCy gives a *white curdy* precipitate of **argentic cyanide**, AgCy, soluble in excess of the reagent; insoluble in dilute nitric acid; soluble in ammonic hydrate, but reprecipitated by dilute nitric acid; soluble in sodic hyposulphite. The precipitate is decomposed by concentrated boiling nitric acid; it is decomposed also when heated by itself in a porcelain crucible to *paracyanide*, metallic silver, and cyanogen gas (DISTINCTION FROM AgCl, AgI, AND AgBr).

Place a bright and clean strip of copper into a solution of argentic nitrate. The copper becomes rapidly covered with a lustrous coating of metallic silver; and the solution, after a time, gives no more precipitate with hydrochloric acid. The silver is deposited on the copper in the metallic state, and the solution contains now $\mathbf{N}_2O_4Cuo''$: an equivalent quantity of copper (63·5 by weight of copper for every 216 of silver) having been dissolved.

Place a small globule of mercury into a concentrated solution of argentic nitrate on a watch glass. The globule of mercury becomes rapidly covered with a crystalline mass, resembling some vegetable growth, termed *arborescence.* After a time the whole of the silver becomes removed from the solution, and the solution contains in the place of the argentic nitrate, mercuric nitrate $\mathbf{N}_2O_4Hgo''$. Metallic silver is precipitated and forms with the mercury an amalgam which is crystalline. This crystalline mass is termed a *silver tree* (*arbor Dianæ*).

Strips of the metals Zn, Fe, Sn, Sb, Pb may likewise be employed for the precipitation of metallic silver.

These changes illustrate the action of the more electropositive metals upon solutions of less electropositive metals, induced by voltaic electricity. They come under the third class of chemical changes, viz., *displacement of one element by another element.*

Take a clear solution of one part of grape sugar and 6—8 parts of distilled water, and a somewhat dilute solution of argentic nitrate. Heat the latter in a test-tube, nearly to boiling, and add the grape-sugar solution. The liquid becomes at once turbid, and a greyish white powder of metallic silver falls to the bottom; or a yellowish white metallic deposit forms on the sides of the test-tube which, on rubbing with a glass rod, shows bright streaks of metallic silver. The metallic silver can be filtered off and fused on charcoal, before the blowpipe, to a brilliant globule.

The cause of the reduction of the argentic salt must evidently be sought for in the grape sugar. We have seen that argentic oxide loses its oxygen readily on ignition. Certain organic substances, such as grape sugar, formic acid, and aldehyde, are known to combine eagerly with oxygen, and the $\mathbf{O}Ag_2$ (in two molecules of $\mathbf{N}O_2Ago$) parts with its oxygen and yields a deposit of metallic silver.

This reaction has found an important practical application in the manufacture of looking-glasses, etc.

The silver in the argentic nitrate is displaced by hydrogen from the organic bodies, $\mathbf{N}O_2Ho$ being left in solution, $\mathbf{C}O_2$ and $\mathbf{O}H_2$—the two ultimate products of oxidation of organic matter—being formed by the oxidation of the organic substances.

Ignite a few crystals of argentic acetate, $\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}OAgo\end{array}\right.$ in a covered porcelain crucible. Heat gently at first, and strongly, as soon as no more fumes are given off. A mass of frosted silver is left, having the shape of the original crystals.

QUESTIONS AND EXERCISES.

1. How is argentic nitrate prepared?
2. Why do HCl, HI, etc., precipitate silver from its solutions?
3. What change takes place when *silver glance* is roasted in a tube?
4. How is Ag separated from Pb in the dry way?
5. Write out the equations for the reactions of silver in the wet way?
6. Give the graphic formulæ for *silver glance, dark red silver ore, proustite*, and *fahl ore.*
7. How much NaCl will be required to convert 1·5 grm. of $\mathbf{N}O_2Ago$ into AgCl?
8. A dilute solution of hydrochloric acid (containing ·00365 grm. of the acid in one cubic centimetre of the solution) is precipitated with $\mathbf{N}O_2Ago$. How much AgCl by weight do we get from 150 c.c. of the acid solution?
9. How much metallic copper is required to precipitate 1 grm. of argentic nitrate?
10. What is the percentage composition of argentic acetate, $\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}OAgo\end{array}\right.$ and how much silver will be left, when ·451 grm. of acetate is ignited?
11. How is argentic nitrate converted into sulphate, and how much of the latter salt can be prepared from 10 grms. of argentic nitrate?
12. What change does AgCy undergo upon ignition?

2. **LEAD**, Pb'' and ^{iv}.—Occurs in nature chiefly in combination with SULPHUR, as $\mathbf{Pb}S''$ in *galena;* also as CARBONATE, in *lead spar* or *white lead ore*, $\mathbf{C}OPbo''$; as SULPHATE, in *lead vitriol*, $\mathbf{S}O_2Pbo''$, in *leadhillite*, $\begin{array}{l}\mathbf{C}O\\ \mathbf{C}O\\ \mathbf{C}O\\ \mathbf{S}O_2\end{array}\begin{array}{l}Pbo''\\ Pbo''Pbo''\\ Pbo''\end{array}$, and in *lanarkite*, $\begin{array}{l}\mathbf{C}O\\ \mathbf{S}O_2\end{array}Pbo''_2$; as OXY-

CHLORIDE, in *mendipite*, $\left\{\begin{matrix}\mathbf{Pb}Cl\\ O\\ Pb''\\ \mathbf{Pb}Cl\end{matrix}\right.$; as PHOSPHATE and OXYCHLORIDE, in *pyromorphite*, $\mathbf{P}_3O_3Pbo''_4\left(\begin{matrix}O\\ Cl\end{matrix}Pb''\right)$.

EXAMINATION IN THE DRY WAY.

The principal blowpipe reaction consists in reducing these minerals on charcoal to metallic lead, either by themselves, or in conjunction with sodic carbonate, or potassic cyanide, and in the *yellow* incrustation of oxide which they yield, which disappears when heated in the oxidizing flame, imparting a *blue* colour to the flame. The change which takes place when *galena*, $\mathbf{Pb}S$, is heated with sodic carbonate in a crucible, out of contact with air, is expressed by the equation:—

$$7\mathbf{Pb}S + 4\mathbf{C}ONao_2 = 4Pb + \underset{\text{Fusible slag.}}{3\mathbf{Pb}Nas_2 + \mathbf{S}O_2Nao_2} + 4\mathbf{C}O_2;$$

but when heated in contact with air, or in the presence of an oxidizing agent, such as saltpetre, the loss of lead in the slag is avoided, thus:—

$$\mathbf{Pb}Nas_2 + 7O + \mathbf{C}ONao_2 = Pb + 2\mathbf{S}O_2Nao_2 + \mathbf{C}O_2$$

When *galena* is roasted in a glass tube open at both ends, it is converted into $\mathbf{S}O_2Pbo''$, $\mathbf{Pb}O$ and $\mathbf{S}O_2$, thus:—

$$(1)\ \mathbf{Pb}S + O_4 = \mathbf{S}O_2Pbo''.$$
$$(2)\ \mathbf{Pb}S + O_3 = \mathbf{Pb}O + \mathbf{S}O_2.$$

With borax and microcosmic salt, lead compounds give in the outer flame a clear *yellowish* glass (owing to the combination of the $\mathbf{Pb}O$ with the boric or phosphoric acid, and formation of a sodic plumbic borate or phosphate), which is *colourless* when cold.

All lead minerals, especially the antimonial sulpho-salts, *boulangerite*, $\mathbf{Sb}_2Pbs_3$, *bournonite*, $\mathbf{Sb}_2Pbs''_2(Cu_2S''_2)''$, *jamesonite*, $\mathbf{Sb}_4S_3Pbs''Pbs''_2$, and *argentiferous galena* contain more or less silver, as may be ascertained by carefully cupelling the metallic button on charcoal (comp. silver, page 222).

The presence of antimony, arsenic, and sulphur reveals itself, when these ores are heated on charcoal (garlic odour and fumes of $\mathbf{As}_2O_3$, or $\mathbf{Sb}_2O_3$), or in a glass tube open at both ends (white sublimate, fumes and odour of $\mathbf{S}O_2$).

REACTIONS IN THE WET WAY.

For the reactions of lead in the wet way we employ either A SOLUTION OF PLUMBIC NITRATE, $\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Pbo''$, or acetate $\left(\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}O\end{matrix}\right)_2Pbo''\right.$; most other plumbic salts being insoluble in water.

HCl (**group-reagent**) or **soluble chlorides** give, with a not too dilute solution of plumbic salts, a *heavy white* precipitate of **plumbic chloride**, $\mathbf{Pb}Cl_2$, soluble in much cold water, readily in boiling water, from which the plumbic chloride crystallizes out, on cooling, in fine needles; less soluble in solutions containing dilute hydrochloric or nitric acid. Ammonia converts it into a **basic salt**, of the composition, $\mathbf{Pb}HoCl$ (*plumbic chlorohydrate*),—a white powder almost insoluble in water.

NaHo or KHo precipitates **plumbic hydrate**, $\mathbf{Pb}Ho_2$, soluble in excess of the reagent, especially on heating. The $\mathbf{Pb}Ho_2$ must be viewed as acting the part of a weak acid, on combining with the strong alkali base.

AmHo precipitates a *white* **basic salt**, insoluble in excess. The precipitate forms only slowly in a solution of plumbic acetate.

$\mathbf{S}H_2$ precipitates *black* **plumbic sulphide**, $\mathbf{Pb}S$, from acid solutions. If a large excess of hydrochloric acid be present, the precipitate is *reddish brown*, consisting of $\left\{\begin{array}{l}\mathbf{Pb}Cl\\ S\\ \mathbf{Pb}Cl\end{array}\right.$, (*diplumbic sulphodichloride*). On diluting considerably with water, a *black* precipitate is obtained.

$\mathbf{S}Am_2$ or **soluble sulphides** precipitate likewise *black* $\mathbf{Pb}S$, insoluble in dilute acids, alkalies, and alkaline sulphides. Plumbic sulphide is soluble in hot dilute nitric acid, plumbic nitrate being formed with separation of sulphur. Concentrated nitric acid converts it into $\mathbf{S}O_2Pbo''$; the oxidation extends to the sulphur as well as to the lead.

$\mathbf{S}O_2Ho_2$ and **soluble sulphates** precipitate *white* **plumbic sulphate**, $\mathbf{S}O_2Pbo''$, insoluble in water, especially in the presence of excess of dilute sulphuric acid; insoluble also in cold dilute acids, soluble in boiling hydrochloric acid, from which plumbic chloride crystallizes out on cooling; soluble in potassic hydrate, and, lastly, readily soluble in concentrated solutions of certain salts, such as ammonic acetate, or tartrate, in the presence of excess of ammonic hydrate, from which solutions $\mathbf{S}O_2Ho_2$, $\mathbf{S}Am_2$, or $\mathbf{Cr}O_2Ko_2$, precipitate the lead again. Boiling with sodic carbonate converts $\mathbf{S}O_2Pbo''$ into insoluble $\mathbf{C}OPbo''$. Plumbic sulphate separates from dilute aqueous solutions only on the addition of alcohol (methylated spirit).

$\mathbf{Cr}O_2Ko_2$ precipitates *yellow* **plumbic chromate**, $\mathbf{Cr}O_2Pbo''$ (*chrome yellow*), readily soluble in potassic or sodic hydrate; difficultly soluble in dilute nitric acid, insoluble in acetic acid..

$\mathbf{C}ONao_2$, as well as $\mathbf{C}OKo_2$ and $\mathbf{C}OAmo_2$, give a *white* precipitate of a **basic carbonate** (*white lead*) of varying composition, usually considered to contain two molecules of plumbic carbonate and one molecule of plumbic hydrate, viz., $\begin{matrix}\mathbf{C}O(OPbHo)\\ \mathbf{C}O(OPbHo)\end{matrix}Pbo''$ (*triplumbic dihydrate carbonate*), insoluble in water and in potassic cyanide.

KI gives a *yellow* precipitate of **plumbic iodide**, $\mathbf{Pb}I_2$, soluble in excess of the reagent; also soluble in much water, from which it separates, on cooling, in beautiful golden yellow scales.

KCy precipitates *white* **plumbic cyanide**, $\mathbf{Pb}Cy_2$, insoluble in excess, soluble in dilute nitric acid.

Soluble *phosphates*, *arsenites* and *arseniates*, *silicates*, *borates*, *oxalates*, *tartrates*, *citrates*, *ferro- and ferricyanides* give precipitates with plumbic salts, which are insoluble in water, but soluble in dilute nitric acid. These precipitates possess, however, only a secondary interest.

Metallic iron or zinc precipitates lead from its salts. This is seen very strikingly on dissolving a few ounces of plumbic acetate (*sugar of lead*) in distilled water, with the addition of a little acetic acid, and suspending in the solution a piece of zinc from a thread. The zinc becomes covered with a beautiful crystalline deposit of metallic lead, which increases rapidly, if the solution be left undisturbed, and acquires the appearance of a branch of a tree (*arbor Saturni*). The metallic structure can be preserved for days in unaltered beauty. On removing the precipitated lead from the piece of zinc, the latter is found much corroded and considerably diminished in size and weight. The lead may be collected on a filter and washed with water, dried and fused in a crucible, under a covering of borax, to a bright metallic button. A quantity of zinc, atomically equivalent in weight to the precipitated lead (*i.e.*, 65 parts by weight of zinc for every 207 of lead) must have dissolved, and is found in the solution, in the form of zincic acetate. The atomic weights of Zn (65) and Pb (207) can be determined roughly, by weighing the metallic zinc, before and after immersion, as well as the precipitated lead.

Heat a little *red lead*, $\mathbf{Pb}_3O_4$, in a small porcelain crucible. The colour changes to yellow. Repeat the experiment by heating another portion in a test-tube, to which a delivery-tube is attached. A gas is given off, which may be collected in the usual manner over water. The residue is dark yellow, and on cooling turns bright yellow. It consists of plumbic oxide, $\mathbf{Pb}O$ (*litharge*), and the gas is oxygen, as can readily be ascertained, by introducing a glowing splinter of wood into it, $\mathbf{Pb}_3O_4 = 3\mathbf{Pb}O + O$.

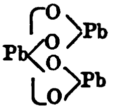
Treat a little $\mathbf{Pb}_3O_4$ with dilute hydrochloric acid in a test-tube, and heat gently. A greenish yellow gas comes off, and the *red lead* dissolves to plumbic chloride. The gas is readily recognized by its odour as chlorine:—

$$\mathbf{Pb}_3O_4 + 8HCl = 3\mathbf{Pb}Cl_2 + Cl_2 + 4\mathbf{O}H_2.$$

Treat another portion of *red lead* with dilute nitric acid. The red colour changes to brown—the colour of plumbic dioxide, $\mathbf{Pb}O_2$. The reaction is expressed by the equation—

$$\mathbf{Pb}_3O_4 + 4\mathbf{N}O_2Ho = 2\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Pbo'' + \mathbf{Pb}O_2 + 2\mathbf{O}H_2.$$

Lead can thus combine either with one or two atoms of oxygen to form $\mathbf{Pb}O$ or $\mathbf{Pb}O_2$; it can exist in the dyad or tetrad condition (Pb'' and Pb^{iv}), and *red lead* is obviously composed of two oxides of $\mathbf{Pb}^{iv}O_2 + 2\mathbf{Pb}''O$. The plumbic dioxide in *red lead* yields the oxygen. It is written graphically:—

$\mathbf{Pb}^{iv}Pbo''_2 =$  (Triplumbic tetroxide).

The minerals *plattnerite*, $\mathbf{Pb}O_2$, and *minium*, $\mathbf{Pb}_3O_4$, represent the corresponding natural oxides.

It is evident from the above experiments, that lead occurs more frequently in the dyad than in the tetrad condition.

$\mathbf{S}O_2Ho_2$ forms with $\mathbf{Pb}O_2$ a sulphate, oxygen being given off.

$\mathbf{Pb}O_2$ absorbs sulphurous anhydride abundantly, forming $\mathbf{S}O_2Pbo''$.

HCl liberates chlorine from plumbic dioxide.

Minium, or ***red lead***, and the brown plumbic dioxide are powerful *oxidizing* agents. They furnish us likewise with ready means for preparing chlorine gas.

QUESTIONS AND EXERCISES.

1. Calculate the percentage composition of plumbic acetate.
2. How much oxygen by weight and by volume (at 0° C. and 760 mm.) can be obtained from 30 grms. of *red lead?*
3. Write out the symbolic equations for the reactions of lead in the wet way.
4. How can Pb be separated from Ag, in the wet way?—1st, by using hydrochloric acid; 2nd, potassic cyanide; 3rd, sulphuric acid, as a precipitant.
5. Give graphic formulæ for *white lead*, *red lead*, plumbic acetate, *mendipite*, plumbic chlorohydrate, plumbic nitrate and chromate, diplumbic sulphodichloride.
6. How much HCl by weight will be required to decompose 10 grms. of *red lead;* and how much chlorine gas will be evolved—1st, by weight; 2nd, by volume at 0° C. and 760 mm. pressure?
7. How would you separate Pb and Sb in type metal?
8. Describe how you would analyze an alloy of 5 parts of lead, 3 parts of tin, and 8 parts of bismuth, a so-called *fusible alloy* melting at 98° C.
9. Calculate the percentage composition of Pb_4Sb (type metal).

3. **MERCURY.**—(Mercurosum) Hg_2''.

We employ A SOLUTION OF MERCUROUS NITRATE, $\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Hg_2o''$.

HCl (**group-reagent**) or **soluble chlorides** give a *white* precipitate of **mercurous chloride**, $'\mathbf{Hg}'_2Cl_2$ (*calomel*), which is insoluble in dilute acids and is blackened by KHo or AmHo, the latter converts it into $'\mathbf{Hg}'_2O$ and *mercurosammonic chloride*, $\mathbf{N}H_2{}'Hg'_2Cl$. Mercurous is converted into mercuric chloride by the addition of chlorine water. Concentrated hydrochloric acid converts it, upon long-continued boiling, into $\mathbf{Hg}Cl_2$ and grey metallic mercury. Nitric acid oxidizes it readily into $\mathbf{Hg}Cl_2$ and $\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Hgo''$, with evolution of nitrous fumes. Dry $'\mathbf{Hg}'_2Cl_2$ sublimes unchanged.

NaHo or KHo gives a *black* precipitate of **mercurous oxide**, $'\mathbf{Hg}'_2O$, insoluble in excess.

AmHo produces a *black* precipitate of **basic dimercurosammonic nitrate**, thus:—

$$2\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Hg_2o'' + 4AmHo = \mathbf{N}_2O_2{}'Hg'_2o''\left[\begin{matrix}NH_2\\ NH_2\end{matrix}{}'Hg'_2O_2\right]''$$

Basic dimercurosammonic nitrate

$$+ 2\mathbf{N}O_2Amo + 3\mathbf{O}H_2.$$

insoluble in excess.

$\mathbf{S}H_2$ precipitates *black* **mercurous sulphide**, $'\mathbf{Hg}'_2S$, insoluble in excess or in dilute acids; soluble in aqua regia or in yellow potassic sulphide. When boiled with concentrated nitric acid, the second atom of mercury in $'\mathbf{Hg}'_2S$ is converted into $\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Hgo''$, and a white compound of mercuric nitrate and sulphide is formed—

$$\left(\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Hgo'', \mathbf{Hg}S\right).$$

$\mathbf{S}Am_2$ produces the same precipitate.

A clean strip of metallic copper precipitates from mercurous solutions metallic mercury, cupric nitrate being left in solution. On gently rubbing the greyish deposit with a piece of wash-leather, the surface becomes bright and shining like silver. *The more electropositive metals,* Cu, Cd, Zn, Fe, Pb, Bi, *precipitate the less electropositive metal* Hg.

$\mathbf{S}OHo_2$, $\mathbf{S}O_2Feo''$, or $\mathbf{Sn}Cl_2$ produces a grey precipitate of metallic mercury. On decanting the liquid and boiling the grey deposit with hydrochloric acid, distinct metallic globules are obtained. The changes may be expressed thus :—

$$\begin{array}{l}\mathbf{N}O_2\\ \mathbf{N}O_2\end{array}Hg_2o'' + \mathbf{S}OHo_2 + \mathbf{O}H_2 = 2Hg + 2\mathbf{N}O_2Ho + \mathbf{S}O_2Ho_2.$$

$$\begin{aligned}3\begin{array}{l}\mathbf{N}O_2\\ \mathbf{N}O_2\end{array}Hg_2o'' + 6\mathbf{S}O_2Feo'' &= 6Hg + 2(\mathbf{S}O_2)_3Fe_2o^{vi}\\ &\quad + (\mathbf{N}O_2)_6Fe_2o^{vi}.\end{aligned}$$

$$\begin{aligned}\begin{array}{l}\mathbf{N}O_2\\ \mathbf{N}O_2\end{array}Hg_2o'' + \mathbf{Sn}Cl_2 + 2HCl &= 2Hg + \mathbf{Sn}Cl_4\\ &\quad + 2\mathbf{N}O_2Ho.\end{aligned}$$

Mercurous salts act thus the part of *oxidizing agents,* when coming in contact with more powerful reducing agents : a property which in conjunction with the *reducing action* which they exert under favourable circumstances, proves clearly that the double atom 'Hg'$_2$ possesses but little chemical affinity for other elements, and *that the compounds which it forms are rather unstable.*

QUESTIONS AND EXERCISES.

1. Write out the graphic formulæ of *calomel,* mercurous nitrate, mercurous oxide, mercurosammonic chloride, basic dimercurosammonic nitrate.
2. Write out equations for the reactions which mercurous compounds give in the wet way.
3. How can mercurous chloride be converted into mercuric chloride? Give equations.
4. How much *calomel* can be manufactured from 20 lbs. of metallic mercury; and how much $\mathbf{S}O_2Ho_2$ and NaCl by weight will be required?
5. Explain the action of metallic mercury upon mercurous nitrate.
6. What is the action of boiling nitric acid upon $\mathbf{Hg}_2S$?
7. In what manner can $\mathbf{Hg}Cl_2$ and $\mathbf{Hg}_2Cl_2$ be distinguished from each other by the reactions in the dry way?
8. State under what conditions mercurous salts play the part of oxidizing, or that of reducing agents.

A method of separating the metals of Group I will readily suggest itself, and a tabular analytical scheme may be drawn up without much difficulty, if we bear in mind :—

1st. The *solubility of* $\mathbf{Pb}Cl_2$ *in boiling water.*

2nd. The *solubility of AgCl in AmHo.*

3rd. The *conversion of the* $\mathbf{Hg}_2Cl_2$ *into black* $\mathbf{N}H_2'Hg_2'Cl$ *by the action of AmHo.*

Table I in the Analytical Tables at the end of the book embodies this method of separation.

PRACTICAL EXERCISES AND QUESTIONS ON GROUP I.

1. Test a sample of *galena* for silver in the dry way.
2. Analyze a sample of *ruby silver* in the dry and in the wet way.
3. You have given to you some precipitated argentic chloride, dilute HCl, and a strip of metallic zinc. How would you prepare pure metallic silver?
4. Analyze a solution, containing ·010 grm. of Ag, as $\mathbf{N}O_2Ago$, ·100 grm. of Hg, as $\mathbf{N}_2O_4Hg_2o''$ and ·010 grm. of Pb, as $\mathbf{N}_2O_4Pbo''$.
5. Describe what takes place when a solution of argentic nitrate, containing about ·010 grm. of Ag, is added to a hot saturated solution of KCl.
6. You have given to you a mixture of *red lead* and *calomel*. What takes place when the mixture is treated with HCl?
7. Analyze a mixture (about ·050 grm.) of *white arsenic* and *corrosive sublimate*, both in the dry and wet way.
8. Test a commercial sample of $\mathbf{Ba}Cl_2$ for lead.
9. Test a sample of *white lead* paint for impurities, insoluble in dilute nitric acid, and examine the acid filtrate by the respective group-reagents.
10. Prepare some pure $\mathbf{N}O_2Ago$ from an alloy of copper and silver.

CHAPTER VII.

REACTIONS OF THE ACIDS.

A. INORGANIC ACIDS.

CARBONIC ANHYDRIDE, CO_2.—Occurs in the atmosphere and in mineral waters. In the combined state it forms a constituent of many minerals, called *carbonates*, which have for the most part been enumerated, in speaking of the natural compounds in which the different metals occur.

REACTIONS IN THE DRY WAY.

On ignition some carbonates undergo changes, others remain unchanged. The carbonates of the fixed alkali metals are not decomposed by the strongest heat. The carbonates of all other metals are decomposed more or less readily into oxides (or metals), carbonic anhydride (and oxygen) being given off. Baric and strontic carbonates require the strongest white heat for their decomposition; calcic carbonate requires a strong red heat. All the others are readily decomposed on heating. The evolved carbonic anhydride is a colourless and almost odourless gas, heavier than air, and can be poured from one vessel into another. When poured or passed into a test-tube containing lime- or baryta-water, a white precipitate is obtained, owing to the combination of the carbonic anhydride with the caustic alkaline earthy bases.

REACTIONS IN THE WET WAY.

All normal carbonates may be divided into—

1st. *Carbonates which are soluble in water*, consisting of the carbonates of the alkali metals and possessing an alkaline reaction.

2nd. *Carbonates which are insoluble in water*, a few of which are, however, soluble in carbonic anhydride, with formation of acid carbonates, such as the carbonates of Ba, Sr, Ca, Mg, Fe'', Mn''.

All carbonates are *decomposed* by dilute acids,—organic or mineral (with the exception of HCy and SH_2). The decomposition is marked by strong effervescence and evolution of CO_2. (A few native carbonates, such as *spathose iron ore*, and *dolomite*, require the application of heat.) On passing the evolved gas into a solution of caustic lime or baryta, the carbonic anhydride becomes once more fixed, and the formation of a white precipitate (soluble in excess of the gas) confirms the presence of CO_2.

Metallic sulphites, sulphides, and nitrites are likewise decomposed by dilute acids with evolution of a gas; but the evolved SO_2, SH_2, or N_2O_3 gases are readily recognized by their characteristic odour or colour. In order to recognize CO_2 in the presence of SO_2 or SH_2, the gaseous mixture is first passed into a solution of an alkaline chromate mixed with an acid, or into bromine water, or a solution of a cupric or ferric salt, and then through lime- or baryta-water.

QUESTIONS AND EXERCISES.

1. How would you prove experimentally the presence of carbonic anhydride, 1st, in spring water; 2nd, in atmospheric air; 3rd, in white lead; 4th, in coal gas?
2. Classify all metallic carbonates according to their respective deportment, 1st, on ignition; 2nd, on treatment with water; 3rd, in contact with excess of CO_2.
3. What change takes place when tartaric acid and hydric potassic carbonate are mixed together?
4. Give instances of normal and acid carbonates.
5. Which is the most characteristic reaction for CO_2?
6. How would you recognize the presence of CO_2 in a gaseous mixture, containing SO_2 and CO_2, or SH_2 and CO_2?
7. How much CO_2, by weight and by volume, can be obtained from 1·235 grm. of $COCao''$?
8. What change takes place, 1st, when a current of CO_2 is passed through cold water in which finely divided chalk is suspended; and 2nd, when the liquid is heated to boiling, subsequent to the passing of the gas?
9. Explain the occurrence of CO_2 in mineral waters and in atmospheric air.
10. Explain the effect of boiling upon most spring waters.
11. What is the usual composition of boiler deposits, and how would you propose to prevent them?
12. Explain what is meant by *temporary hardness* in waters.

SULPHURIC ACID, SO_2Ho_2.—This is one of the most powerful acids, for it is capable of displacing, in the wet way (with few exceptions), all other acids from saline compounds. It forms with bases a series of very important salts,—the sulphates, most of which have already been enumerated on treating of the natural compounds of the various metals.

REACTIONS IN THE DRY WAY.

On heating a sulphate on charcoal, in the reducing flame, together with $\mathbf{C}ONao_2$ (free from sulphate), sodic sulphide is formed, thus:—

$$\mathbf{S}O_2Mgo'' + 2C + \mathbf{C}ONao_2 = \mathbf{S}Na_2 + \mathbf{Mg}O + 3\mathbf{C}O_2.$$

The fused mass gives off $\mathbf{S}H_2$, when treated with a strong acid (HCl), readily recognized by its odour. When placed on a bright silver coin and moistened with a drop of water, it produces a black stain of argentic sulphide. This reaction applies, however, to all sulphur acids, without exception, and it is impossible to prove thereby the presence of $\mathbf{S}O_2Ho_2$ any more than that of some other (lower) oxide of sulphur.

Heated by themselves, the sulphates of the alkalies and alkaline earthy metals, as well as of lead, are not decomposed. All other sulphates become decomposed more or less speedily on ignition, giving off sulphuric or sulphurous anhydride and oxygen, according to the nature of the metal, *e.g.*:—

$$2\mathbf{S}O_2Feo'' = \mathbf{Fe}_2O_3 + \mathbf{S}O_3 + \mathbf{S}O_2.$$
$$\mathbf{S}O_2Cuo'' = \mathbf{Cu}O + \mathbf{S}O_2 + O.$$

REACTIONS IN THE WET WAY.

A SOLUTION OF POTASSIC SULPHATE, $\mathbf{S}O_2Ko_2$, may be employed.

Sulphuric acid forms normal and acid sulphates, which are mostly soluble in water, the exceptions being baric, strontic, calcic, and plumbic sulphates. (A few basic sulphates are insoluble in water, but soluble in acids.)

$\mathbf{Ba}Cl_2$ or $\mathbf{N}_2O_4Bao''$ gives a *white* finely divided precipitate of **baric sulphate,** $\mathbf{S}O_2Bao''$, insoluble in dilute acids. Care must be taken not to have too much free hydrochloric or nitric acid present, lest any of the baric salts be precipitated: baric chloride and nitrate being much less soluble in strong acids than in water. If a very dilute solution of a sulphate has to be precipitated, the solution should be heated to boiling, and allowed to stand for some time after the addition of the baric salt.

This reaction distinguishes $\mathbf{S}O_2Ho_2$ from all other acids, except hydrofluosilicic acid, 2HF, $\mathbf{Si}F_4$, and selenic acid, $\mathbf{Se}O_2Ho_2$, which also form insoluble baric salts.

Soluble salts of strontium, calcium, and lead produce *white* precipitates of **strontic, calcic,** and **plumbic sulphates,** which are more or less soluble in large quantities of water: $\mathbf{S}O_2Cao''$ being the most soluble (500 parts of water), $\mathbf{S}O_2Sro''$ dissolving in 9,000 parts of water, and $\mathbf{S}O_2Pbo''$ in 22,000 parts of water only.

Since baric salts answer every purpose, recourse is rarely had to these reactions in order to detect sulphuric acid. The addition of alcohol (methylated spirit), ensures the complete precipitation of strontic, calcic, and plumbic sulphates. Most soluble sulphates can, in fact, be precipitated from their aqueous solutions by the addition of strong alcohol.

In order to detect free sulphuric acid, by itself, or in the presence of a sulphate, the solution is evaporated to dryness on a water-bath, together with a little cane sugar. A blackened or charred residue indicates *free* sulphuric acid, as no other acid is capable of decomposing cane sugar in like manner.

An *insoluble sulphate* can be decomposed by continued boiling with a concentrated solution of an alkaline carbonate; more readily, however, by fusion with alkaline carbonates (fusion mixture), into a soluble alkaline sulphate, and an insoluble carbonate or oxide of the metal, thus:—

$$2\mathbf{S}O_2Bao'' + \mathbf{C}ONao_2,\mathbf{C}OKo_2 = \mathbf{S}O_2Nao_2,\mathbf{S}O_2Ko_2 + 2\mathbf{C}OBao''.$$

$$2\mathbf{S}O_2Pbo'' + \mathbf{C}ONao_2,\mathbf{C}OKo_2 = \mathbf{S}O_2Nao_2,\mathbf{S}O_2Ko_2 + 2\mathbf{Pb}O + 2\mathbf{C}O_2.$$

The fused mass is extracted with boiling water, and the insoluble carbonate or oxide separated by filtration from the soluble alkaline sulphate. The residue is examined as usual for base, and the solution for sulphuric acid, by acidulating with dilute hydrochloric acid (in order to destroy the excess of alkaline carbonates), and adding $\mathbf{Ba}Cl_2$. Calcic sulphate dissolves in ammonic sulphate and excess of AmHo; plumbic sulphate in ammonic acetate or tartrate, or in sodic hyposulphite..

QUESTIONS AND EXERCISES.

1. Classify all metallic sulphates according to their solubility in water.
2. How are metallic sulphates detected, in the dry way?
3. Explain the action of heat upon the different metallic sulphates.
4. How is free sulphuric acid detected?
5. How would you detect a soluble sulphate, in the presence of free sulphuric acid?
6. Describe shortly in what manner $\mathbf{S}O_2Bao''$, $\mathbf{S}O_2Sro''$, $\mathbf{S}O_2Cao''$, and $\mathbf{S}O_2Pbo''$ differ from each other with regard to their solubility in water, and their respective deportment with various other solvents.
7. How are insoluble sulphates examined qualitatively?
8. 1·648 grm. of a sample of *soda-ash* yielded ·234 grm. of $\mathbf{S}O_2Bao''$; what is the percentage of sodic sulphate in the ash?

SULPHUROUS ACID, $\mathbf{S}OHo_2$.—Obtained as gaseous anhydride, $\mathbf{S}O_2$, whenever sulphur is burnt in air or oxygen, or when metallic sulphides (*pyrites*, *blende*, *galena*, etc.), are roasted with free access of air; also by the partial deoxidation of sulphuric acid by means of metals, such as Cu, Hg, Ag (comp. Exp. 64), of charcoal and various organic bodies, of sulphur, etc. The gas is readily soluble in water, forming sulphurous acid, $\mathbf{S}OHo_2$, which combines with bases, and forms a series of salts, normal or acid, termed sulphites: compounds strongly characterized by the tendency which they exhibit to absorb oxygen and to become converted into sulphates. This property causes $\mathbf{S}OHo_2$, or sulphites, to be of considerable interest.

REACTIONS IN THE DRY WAY.

Sulphurous anhydride is recognized by its characteristic odour, the odour of burning sulphur. It combines readily with metallic peroxides, such as $\mathbf{Mn}O_2$, $\mathbf{Pb}O_2$, with formation of manganous and plumbic sulphates. In order, therefore, to remove $\mathbf{S}O_2$ from a gaseous mixture, the latter is usually passed over $\mathbf{Pb}O_2$.

Many solid sulphites are decomposed by heat into sulphates and sulphides, thus:—

$$4\mathbf{S}ONao_2 = 3\mathbf{S}O_2Nao_2 + \mathbf{S}Na_2.$$

The earthy sulphites break up into oxides and sulphurous anhydride.

REACTIONS IN THE WET WAY.

A SOLUTION OF SODIC SULPHITE, $\mathbf{S}ONao_2$, may be employed.

Sulphites are examined by liberating sulphurous anhydride by means of strong sulphuric or hydrochloric acid, the gas being readily recognized by its characteristic pungent odour.

The only sulphites soluble in water are the alkaline sulphites. Normal baric, strontic, calcic, and magnesic sulphites are insoluble in water, but are dissolved, to a great extent, by a solution of sulphurous acid, with formation of acid sulphites, from which the normal salts are reprecipitated on boiling. They are also soluble in dilute hydrochloric acid (with partial decomposition); but on the addition of an oxidizing agent, such as chlorine water, free iodine, sodic hypochlorite, nitric acid, etc., they are immediately precipitated as insoluble sulphates ($\mathbf{S}O_2Mgo''$ excepted).

Sulphites generally contain sulphates. A precipitate consisting of baric sulphate is, therefore, frequently obtained on adding $\mathbf{Ba}Cl_2$ to an acidulated solution of a soluble, or to a dilute hydrochloric acid solution of an insoluble sulphite.

On filtering off the precipitate, and adding chlorine water to the filtrate, a further precipitate is obtained, showing the presence of a sulphite.

Traces of sulphurous acid are distinguished with difficulty by the odour alone, and it is preferable, therefore, to make use of the deoxidizing, as well as oxidizing action which the acid can exert.

1. *Sulphurous acid acts as a powerful reducing agent.*

$\mathbf{N}O_2Ago$ gives with sodic sulphite a *white* precipitate of **argentic sulphite**, $\mathbf{S}OAgo_2$, soluble in excess of the alkaline sulphite, which blackens on heating, owing to the precipitation of metallic silver, and conversion of the $\mathbf{S}OHo_2$ into $\mathbf{S}O_2Ho_2$, according to the equation:—

$$\mathbf{S}OAgo_2 + \mathbf{O}H_2 = Ag_2 + \mathbf{S}O_2Ho_2.$$

$\mathbf{N}_2O_4Hg_2o''$ produces a *grey* precipitate of **metallic mercury**, thus:—

$$\mathbf{S}OHg_2o'' + \mathbf{O}H_2 = Hg_2 + \mathbf{S}O_2Ho_2.$$

The instances of the reducing action of sulphurous acid are very numerous; we need only refer here to its action upon solutions of $\mathbf{Au}Cl_3$, $\mathbf{Cr}O_2Ho_2$, $\mathbf{Fe}_2Cl_6$, and others, already noticed under the respective metals.

2. Under favourable circumstances *sulphurous acid acts as an oxidizing agent*, especially when brought in contact with other *more powerful* reducing agents, such as nascent hydrogen, $\mathbf{S}H_2$, $\mathbf{Sn}Cl_2$, etc. Thus, by introducing the least trace of $\mathbf{S}OHo_2$, or a sulphite, into a flask, in which hydrogen is generated from zinc and hydrochloric acid, $\mathbf{S}H_2$ is immediately evolved, together with the hydrogen, and may be recognized by its odour and action upon lead paper. The change is expressed as follows:—

$$\mathbf{S}O_2 + 3H_2 = \mathbf{S}H_2 + 2\mathbf{O}H_2.$$

$\mathbf{S}O_2$ and $\mathbf{S}H_2$ give rise to the formation of pentathionic acid, $\left\{\begin{array}{l}\mathbf{S}^{vi}O_2Ho\\ S''_3\\ \mathbf{S}^{vi}O_2Ho\end{array}\right.$ with precipitation of *white* sulphur, according to the equation:—

$$5\mathbf{S}O_2 + 5\mathbf{S}H_2 = \left\{\begin{array}{l}\mathbf{S}O_2Ho\\ S_3\\ \mathbf{S}O_2Ho\end{array}\right. + S_5 + 4\mathbf{O}H_2.$$

Sulphurous acid added to stannous chloride in the presence of hydrochloric acid, gradually precipitates yellow $\mathbf{Sn}S_2$. The hydrogen of the HCl acts as the reducing agent, and is detached from the chlorine by the simultaneous action of the $\mathbf{Sn}Cl_2$ and $\mathbf{S}O_2$, the one eager to combine with chlorine, the other capable of yielding oxygen to the hydrogen, to form water, and ultimately sulphur, to form $\mathbf{S}H_2$, which in its turn acts upon the stannic chloride, $\mathbf{Sn}Cl_4$ (or $\mathbf{Sn}Cl_2$) to form yellow stannic sulphide, $\mathbf{Sn}S_2$ (or brown $\mathbf{Sn}S$). The following equations express the changes:—

$$(1)\quad \mathbf{S}OHo_2 + 3\mathbf{Sn}Cl_2 + 6HCl = 3\mathbf{Sn}Cl_4 + \mathbf{S}H_2 + 3\mathbf{O}H_2.$$

$$(2)\quad \mathbf{Sn}Cl_4 + 2\mathbf{S}H_2 = \underset{\text{Yellow stannic sulphide.}}{\mathbf{Sn}S_2} + 4HCl.$$

QUESTIONS AND EXERCISES.

1. Describe different methods of preparing sulphurous anhydride.
2. How would you prepare normal and acid potassic sulphite?
3. What is the action of heat upon sulphites?
4. Which sulphites are soluble and which are insoluble in water?
5. Give illustrations of the reducing action of sulphurous acid or of soluble sulphites.
6. Explain under what circumstances $\mathbf{S}O_2$ can act as an oxidizing agent; give instances of such action.
7. How would you distinguish $\mathbf{S}OHo_2$, in the presence of $\mathbf{S}O_2Ho_2$?
8. What changes take place when a mixture of dipotassic dichromate and sodic sulphite is treated with concentrated HCl? Give equations.
9. How would you fix the $\mathbf{S}O_2$, produced by the combustion of carbonic disulphide contained in coal gas?

HYPOSULPHUROUS ACID, $\mathbf{S}SOHo_2$ (*sulpho-sulphuric acid*).—This acid has never been obtained in the free state. Combined with soda it forms an important salt, viz., sodic hyposulphite (the *hypo* of the photographer), obtained by boiling a solution of sodic sulphite with sulphur, or by the oxidation of an alkaline persulphide in contact with the air.

REACTIONS IN THE DRY WAY.

All hyposulphites are decomposed on ignition. Alkaline hyposulphites leave a polysulphide and a sulphate, thus :

$$4(\mathbf{S}SONao_2) = \mathbf{S}_5Na_2 + 3\mathbf{S}O_2Nao_2.$$

Others yield sulphides or sulphates with evolution of $\mathbf{S}O_2$, owing to the oxidation of a portion of the sulphur.

REACTIONS IN THE WET WAY.

A SOLUTION OF SODIC HYPOSULPHITE, $\mathbf{S}SONao'_2$, is employed.

Most hyposulphites are soluble in water (baric hyposulphite is difficultly soluble in cold water), and their solutions may, with few exceptions, be boiled without decomposition. Calcic hyposulphite is gradually decomposed on boiling, the precipitate consisting of $\mathbf{S}O_2Cao''$ and S. The same decomposition takes place more speedily, when hyposulphites are treated with sulphuric or hydrochloric acid. Sulphurous anhydride is evolved with separation of sulphur. The precipitated sulphur is yellow, and not white, as is usually the case, when sulphur separates in chemical reactions. *This change characterizes hyposulphites.*

The same instability of the sulphur atom, occupying the place of an atom of oxygen in $\mathbf{S}O_2Ho_2$, is observed, when hyposulphites come in contact with salts, whose metals form with sulphur insoluble sulphides.

$\mathbf{N}O_2Ago$ gives a *white* precipitate of **argentic hyposulphite,** $\mathbf{S}SOAgo_2$, soluble in sodic hyposulphite, which speedily turns yellow, then brown, and lastly black ($\mathbf{S}Ag_2$), especially on the application of heat, thus:—$\mathbf{S}SOAgo_2 + \mathbf{O}H_2 = \mathbf{S}Ag_2 + \mathbf{S}O_2Ho_2$

$\mathbf{N}_2O_4Hg_2o''$, and $\left(\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}O\end{matrix}\right.\right)_2Pbo''$ give similar precipitates, decomposed by heat into $\mathbf{Hg}_2S$ or $\mathbf{Pb}S$, and sulphuric acid.

$\mathbf{Sn}Cl_2$ gives a *brown* precipitate of $\mathbf{Sn}S$.

Hyposulphites like sulphites *are readily oxidized*, but yield under certain conditions oxygen to more powerful reducing agents, and become thus *oxidizing* agents.

Free chlorine, sodic hypochlorite, ferric chloride, etc., oxidize hyposulphites completely to sulphates, even in the cold, thus :—

$$\mathbf{S}SONao_2 + 4Cl_2 + 5\mathbf{O}H_2 = 2\mathbf{S}O_2HoNao + 8HCl.$$
$$\mathbf{S}SONao_2 + 4ClNao + \mathbf{O}H_2 = 2\mathbf{S}O_2HoNao + 4NaCl.$$

$\mathbf{S}SONao_2$ gives with $\mathbf{Fe}_2Cl_6$ at first a reddish violet coloration (DIFFERENCE BETWEEN SULPHITES AND HYPOSULPHITES), but on standing, the solution is slowly decolorized (more rapidly on heating), with formation of $\mathbf{Fe}Cl_2$, thus :—

$$\mathbf{S}SONao_2 + 4\mathbf{Fe}_2Cl_6 + 5\mathbf{O}H_2 = 2\mathbf{S}O_2HoNao + 8\mathbf{Fe}Cl_2 + 8HCl.$$

Nascent hydrogen *reduces* hyposulphites to sulphides, which evolve with the acid sulphuretted hydrogen:—

$$\mathbf{S}SONao_2 + 4H_2 + 2HCl = 2\mathbf{S}H_2 + \mathbf{S}OH_2 + 2NaCl.$$

Sodic hyposulphite is a useful solvent for AgCl (hence its application in photography), $\mathbf{Hg}_2Cl_2$ and $\mathbf{S}O_2Pbo''$. Calcic hyposulphite, $\mathbf{S}SOCao''$, has also found an interesting application, as an agent for removing the last traces of chlorine in the bleaching of paper pulp, and from fabrics bleached by means of *bleaching powder*, $\mathbf{Ca}(OCl)Cl$, to prevent their deterioration by the traces of chlorine which they are apt to retain. It has on that account received the name of *antichlor*. The free hydrochloric acid which is formed in the reaction is neutralized by passing the fabrics through a weak alkaline bath.

The property of sodic hyposulphite of dissolving AgCl has found an important metallurgical application in the removal of silver from poor argentiferous ores, after they have undergone the process of roasting with common salt, which converts the silver into AgCl, insoluble in water.

Besides the three oxygen acids of sulphur just described, there are others, such as *dithionic*, $\left\{\begin{array}{l}\mathbf{S}O_2Ho\\ \mathbf{S}O_2Ho\end{array}\right.$, *trithionic*, $\left\{\begin{array}{l}\mathbf{S}O_2Ho\\ S\\ \mathbf{S}O_2Ho\end{array}\right.$, *tetrathionic*, $\left\{\begin{array}{l}\mathbf{S}O_2Ho\\ S_2\\ \mathbf{S}O_2Ho\end{array}\right.$ and *pentathionic acids*, $\left\{\begin{array}{l}\mathbf{S}O_2Ho\\ S_3\\ \mathbf{S}O_2Ho\end{array}\right.$, which occur but rarely, and resemble one another considerably in their reactions. Their consideration must be reserved for a more extensive course of study.

QUESTIONS AND EXERCISES.

1. How is sodic hyposulphite prepared?
2. How would you prepare ferrous, aluminic, chromic, and manganous hyposulphites?
3. How are hyposulphites affected by ignition?
4. What change takes place, when a solution of calcic hyposulphite is boiled, 1st, by itself, 2nd, when it is treated with HCl?
5. Explain the action of sodic hyposulphite upon plumbic, argentic, mercurous and stannous salts.
6. Give instances, 1st, of the reducing action, and 2nd, of the oxidizing action of hyposulphites.
7. Explain the term *antichlor*.
8. State what application sodic hyposulphite has found in photography and in metallurgy.
9. Give graphic formulæ for sulphosulphuric, dithionic, trithionic, tetrathionic and pentathionic acids.
10. How would you recognize a sulphite in the presence of a hyposulphite?
11. How would you separate a hyposulphite from a sulphate?
12. Calculate the percentage composition of sodic hyposulphite ($\mathbf{S}SONao_2 + 5Aq$).

HYDROSULPHURIC ACID, $\mathbf{S}H_2$.—Obtained as a colourless gas by the decomposition of metallic sulphides, such as $\mathbf{Fe}S$, $\mathbf{Zn}S$, $\mathbf{Sb}_2S_3$, by means of sulphuric or hydrochloric acid. It is characterized by a most fœtid odour, resembling that of rotten eggs. It is absorbed by cold water, forming sulphuretted hydrogen water or hydrosulphuric acid, which reddens blue litmus-paper feebly. $\mathbf{S}H_2$ exchanges its sulphur for the oxygen of most metallic oxides, both in the dry and wet way, forming water and metallic sulphides. It is on this account a most valuable reagent. Many of these sulphides, for example, *iron pyrites*, *galena*, *cinnabar*, *zinc blende*, exist in nature in vast masses.

REACTIONS IN THE DRY WAY.

Metallic sulphides are acted upon in various ways, when submitted to heat. Some are decomposed, when heated in a close vessel, into metal and sulphur, *e.g.*, $\mathbf{Au}_2S_3$; some sulphides, such as $\mathbf{Pt}S_2$, $\mathbf{Fe}S_2$, $\mathbf{Sb}_2S_5$, $\mathbf{Sn}S_2$ $\mathbf{Pb}S$ yield up a portion of their sulphur and are reduced to $\mathbf{Pt}S$, $\mathbf{Fe}_3S_4$, $\mathbf{Sb}_2S_3$, $\mathbf{Sn}S$, $\mathbf{Pb}_2S$; others sublime without decomposition, such as $\mathbf{As}_2S_3$ (*orpiment*), $\mathbf{Hg}S$ (*cinnabar*). The greater number of metallic sulphides remain, however, undecomposed, when heated out of contact with atmospheric air.

Most sulphides undergo a change, when roasted in a tube open at both ends. $\mathbf{S}Ag_2$ leaves metallic silver (usually also a little $\mathbf{S}O_2Ago_2$), the sulphur by combining with oxygen, passes off as $\mathbf{S}O_2$; some sulphides leave a metallic oxide, *e.g.*, $\mathbf{Sn}S$, $\mathbf{Sb}_2S_3$, $\mathbf{Bi}_2S_3$; others again, such as the sulphides of the alkalies and alkaline earthy metals, are converted into sulphates. Plumbic sulphide (*galena*) is converted into a mixture of oxide and sulphate; cupric sulphide, at a high temperature, yields $\mathbf{S}O_2$ and $\mathbf{Cu}O$; at a lower temperature $\mathbf{S}O_2Cuo''$. $\mathbf{Fe}S$ and other sulphides of the iron group are partially converted into sulphates, which on the application of a stronger heat, lose their acid, leaving metallic oxides. Many native metallic sulphides are distinguished for their metallic lustre, such as *iron* and *copper pyrites*, *galena*, *grey antimony*. The presence of a metallic sulphide cannot, however, be inferred conclusively from the evolution of $\mathbf{S}O_2$, since earthy sulphites are broken up, on ignition, into oxides and sulphurous anhydride.

REACTIONS IN THE WET WAY.

Alkaline and alkaline earthy sulphides are soluble in water ($\mathbf{Ca}S$ and $\mathbf{Mg}S$ are only sparingly soluble). Dilute hydrochloric acid decomposes them readily into metallic chlorides and $\mathbf{S}H_2$. *All other sulphides are insoluble in water.* Many of the latter, such as $\mathbf{Fe}S$, $\mathbf{Mn}S$, $\mathbf{Zn}S$ are decomposed by dilute hydrochloric acid with evolution of sulphuretted hydrogen. Others require concentrated hydrochloric acid, such as $\mathbf{Ni}S$, $\mathbf{Co}S$ (difficultly soluble), $\mathbf{Sb}_2S_3$, $\mathbf{Sn}S_2$, $\mathbf{Pb}S$. Sulphides which are insoluble, or difficultly soluble, in concentrated hydrochloric acid, such as $\mathbf{Bi}_2S_3$, $\mathbf{Cu}S$, $\mathbf{S}Ag_2$, are decomposed by concentrated nitric acid; whilst others, such as $\mathbf{Hg}S$, $\mathbf{Pt}S_2$, $\mathbf{Au}_2S_3$, $\mathbf{As}_2S_3$, dissolve only in aqua regia, or hydrochloric acid and potassic chlorate, with separation of sulphur and formation of $\mathbf{S}O_2Ho_2$, and of a metallic chloride. On dissolving $\mathbf{Pb}S$, $\mathbf{Sn}S_2$, $\mathbf{Sb}_2S_3$ in concentrated nitric, instead of hydrochloric acid, they are converted principally into $\mathbf{S}O_2Pbo''$, $\mathbf{Sn}O_2$, $\mathbf{Sb}_2O_4$.

Others ($\mathbf{Hg}S$ excepted) are gradually oxidized by concentrated nitric acid into sulphates—at first with separation of sulphur, which by prolonged digestion is converted into sulphuric acid.

To detect $\mathbf{S}H_2$ (*in an aqueous solution*) *or a soluble sulphide* (a solution of $\mathbf{S}Am_2$ may be conveniently employed), add a solution of a salt of cadmium, lead or silver, which gives by double decomposition a characteristic precipitate of a metallic sulphide: fine yellow for cadmium, black for plumbic or argentic salts.

To analyze *a sulphide decomposable by hydrochloric acid*, the evolved sulphuretted hydrogen gas is made to act upon lead paper, or is passed through a solution of a plumbic salt. (*Iron pyrites*, $\mathbf{Fe}S_2$, and *copper pyrites*, $\mathbf{Cu}_2S$, $\mathbf{Fe}_2S_3$, give off $\mathbf{S}H_2$ only in the presence of hydrochloric acid and zinc.)

Sulphides which are not decomposed by hydrochloric acid, yield sulphur on treatment with nitric acid or aqua regia, and must be recognized by this and the products of decomposition, such as $\mathbf{Sn}O_2$, $\mathbf{S}O_2Pbo''$, as well as the reactions which they give, when examined in the dry way.

Many native sulphides, such as fahl ore, etc., are expeditiously examined by heating the finely-powdered mineral in a hard glass tube, in a current of dry chlorine gas, when the metals are converted into chlorides and the sulphur into volatile chloride of sulphur, which is decomposed on being passed into water.

To detect a *soluble sulphide in the presence of free* $\mathbf{S}H_2$, add a few drops of a solution of sodic nitroprusside. This reagent does not affect free $\mathbf{S}H_2$, but gives a fine purple colour with the merest traces of soluble sulphides. The colour disappears only after some time.

A mixture containing *a soluble alkaline sulphide*, *hyposulphite*, *sulphite*, or *sulphate* may be examined by adding $\mathbf{C}OCdo''$ to the aqueous solution. Filter, dissolve the excess of $\mathbf{C}OCdo''$ in the precipitate by means of dilute acetic acid; a residue of yellow $\mathbf{Cd}S$ indicates the presence of an alkaline sulphide. Add to the filtrate $\mathbf{Ba}Cl_2$; a precipitate is obtained, consisting of $\mathbf{S}O_2Bao''$ and $\mathbf{S}OBao''$. Filter off; digest the precipitate with dilute hydrochloric acid, and filter. A white residue shows the presence of an alkaline sulphate. Add chlorine water to the filtrate; a precipitate of $\mathbf{S}O_2Bao''$ indicates the presence of an alkaline sulphite. The filtrate from the $\mathbf{Ba}Cl_2$ precipitate is searched for $\mathbf{S}SOHo_2$ by the addition of HCl and boiling. A *yellow* precipitate of sulphur and the odour of $\mathbf{S}O_2$ indicate the presence of a hyposulphite.

To remove $\mathbf{S}H_2$ from a gaseous mixture of $\mathbf{C}O_2$ and $\mathbf{S}H_2$, add a solution of cupric chloride and shake up with the gases; or pass the gases through an ammoniacal solution of argentic nitrate.

QUESTIONS AND EXERCISES.

1. Explain the changes which take place when $\mathbf{S}H_2$ is passed through saline solutions, the metals of which form insoluble sulphides. Give instances.
2. Explain the action of heat upon the different metallic sulphides.
3. Which sulphides are soluble and which are insoluble in water?
4. Explain how certain sulphides are affected by dilute hydrochloric acid, and how by concentrated hydrochloric acid. Give characteristic instances, and express the changes by equations.
5. Describe the most delicate reaction for gaseous $\mathbf{S}H_2$, and state how free $\mathbf{S}H_2$ can be distinguished in the presence of a soluble sulphide.
6. What is the action of nitric acid upon $\mathbf{Zn}S$, $\mathbf{Pb}S$, $\mathbf{Cu}S$, $\mathbf{Sn}S$, $\mathbf{Sb}_2S_3$?

7. How would you prove the presence of an alkaline sulphide, hyposulphite, sulphite, and sulphate in an aqueous solution?
8. State how you would separate $\mathbf{S}H_2$ and $\mathbf{C}O_2$ contained in a gaseous mixture.
9. How can you prove the presence of $\mathbf{S}H_2$ in coal gas?
10. 10 litres of unpurified coal gas yielded ·235 grm. of $\mathbf{CdS}$. What is the percentage of $\mathbf{S}H_2$ in the gas?
11. ·650 grm. of *galena* gave ·532 grm. of $\mathbf{S}O_2Pbo''$. What is the percentage of Pb and of S in the galena?
12. What change takes place when $\mathbf{PtS}_2$, $\mathbf{Sb}_2\mathbf{S}_5$, $\mathbf{FeS}_2$, $\mathbf{As}_2\mathbf{S}_3$, and $\mathbf{HgS}$ are heated with exclusion of air?
13. How would you test for $\mathbf{S}H_2$ in sewer gases?
14. What action has $\mathbf{S}H_2$ upon white lead paint; and how would you propose to remove $\mathbf{PbS}$ from oil paintings, so as to restore the original white colour?
15. How would you detect sulphur in pig iron?
16. Explain the action of chlorine, bromine, and iodine upon $\mathbf{S}H_2$.
17. How is sulphur detected in organic compounds, such as coal?

NITRIC ACID, $\mathbf{N}O_2Ho$.—Obtained as a colourless, highly corrosive, volatile liquid, of a deep yellow colour when it is mixed with nitrous acid, $\mathbf{N}OHo$. It is characterized by the facility with which it parts with its oxygen (comp. Chapter XIV.), and it is this property of which we avail ourselves invariably, when nitric acid or a nitrate has to be detected.

REACTIONS IN THE DRY WAY.

Most nitrates fuse readily when heated. All are decomposed when exposed by themselves to a high temperature. The decomposition varies with the nature of the base; a lower oxide of nitrogen, and oxygen being generally given off. Thus ammonic nitrate, $\mathbf{N}O_2Amo$, breaks up into $\mathbf{O}N_2$ and $\mathbf{O}H_2$; potassic or sodic nitrate into nitrite (always contaminated, however, with nitrate and caustic alkali), with liberation of oxygen and ultimately into oxide—nitrogen and oxygen being given off; others, such as plumbic nitrate, into O and $\mathbf{N}_2O_4$, leaving the oxide of the metal. When heated together with bodies eager to take up oxygen, such as carbon (charcoal or alkaline cyanides), sulphur or phosphorus, the decomposition becomes explosively violent, and nitrogen gas only is left as the remnant of the molecule $\mathbf{N}_2O_5$. (Chlorates explode in like manner, but leave metallic chlorides.)

REACTIONS IN THE WET WAY.

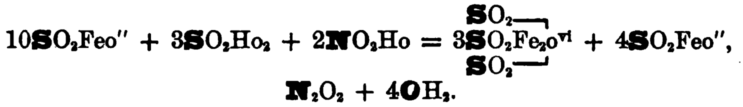
With the exception of a few basic salts, nitrates are readily soluble in water: hence nitric acid cannot be tested in the usual way, by producing precipitates by way of double decomposition. When acted upon by various reducing agents, the deoxidation of the acid may be *partial* (accompanied by the evolution of lower oxides of nitrogen), or *complete* (nitrogen only being left); in which case the nascent nitrogen is capable of combining with hydrogen in the nascent state to form ammonia, $\mathbf{N}H_3$. (Comp. Exp. 69.)

1st. *Reactions in which* $\mathbf{N}O_2Ho$ *is reduced to lower oxides of nitrogen.*

A SOLUTION OF NITRIC ACID OR OF POTASSIC NITRATE, $\mathbf{N}O_2Ko$, may be employed.

$\mathbf{N}O_2Ho$ (or $\mathbf{N}O_2Ko$) is decomposed when heated with concentrated hydrochloric acid (or a chloride when heated with nitric acid). Chloronitric gas, $\mathbf{N}_2O_2Cl_4$, is evolved (comp. p. 86), and the liquid acquires the power of dissolving gold-leaf or platinum foil, which are not soluble in single acids. (Chlorates, bromates, iodates, chromates, and permanganates evolve chlorine when treated with hydrochloric acid; they dissolve gold or platinum, but give off no $\mathbf{N}_2O_2$.)

Add to a dilute solution of ferrous sulphate cautiously its own volume of concentrated sulphuric acid (free from nitric acid), and allow the mixture to cool; then add gradually a solution containing a nitrate. A ring is seen to form at the point of contact of the two layers, of a violet, red, or dark brown colour, according to the quantity of the nitrate present. The coloration is increased by carefully shaking up the fluid, but it disappears on heating. This is owing to the formation of a transient compound of the ferrous salt with $\mathbf{N}_2O_2$, consisting of four molecules of the salt with one molecule of nitric acid ($4\mathbf{S}O_2Feo''$, $\mathbf{N}_2O_2$). The other three atoms of oxygen from two molecules of nitric acid oxidize six molecules of ferrous into three molecules of ferric sulphate, $\mathbf{S}_3O_6Fe_2o^{vi}$. This constitutes one of the most delicate reactions for nitric acid. The change may be expressed thus :—



$$10\mathbf{S}O_2Feo'' + 3\mathbf{S}O_2Ho_2 + 2\mathbf{N}O_2Ho = 3\begin{array}{l}\mathbf{S}O_2\text{—}\\ \mathbf{S}O_2Fe_2o^{vi}\\ \mathbf{S}O_2\text{—}\end{array} + 4\mathbf{S}O_2Feo'',$$
$$\mathbf{N}_2O_2 + 4\mathbf{O}H_2.$$

A solution of $\mathbf{N}O_2Ko$, when added to a solution of indigo in sulphuric acid (sulphindigotic acid), changes the blue colour of the indigo to yellow. (Free chlorine and other oxidizing agents bleach indigo likewise.)

Metallic copper (Ag, Zn, Pb, or Hg) is dissolved by nitric acid with evolution of ruddy fumes, and by $\mathbf{N}O_2Ko$ on the addition of sulphuric acid.

A similar reaction takes place, when copper filings are mixed with a nitrate and hydric potassic sulphate and fused in a test-tube or crucible.

Minute quantities of nitrates found in mineral waters, in rain water, or water draining from arable land, may be detected by first reducing the nitrate to nitrite. This is effected by heating the solution for some time with a little zinc amalgam. On filtering and adding to the filtrate a solution of ferrous salt, a dark brown coloration is obtained; or by adding a drop of a solution of potassic iodide, some freshly prepared starch solution, and a little acetic (or very dilute sulphuric) acid, a fine blue precipitate of iodide of starch is produced, thus:—

$$2\mathbf{N}OKo + 2KI + 2\mathbf{S}O_2Ho_2 = \mathbf{N}_2O_2 + 2\mathbf{S}O_2Ko_2 + I_2 + 2\mathbf{O}H_2.$$

This reaction is exceedingly delicate.

2nd. *Reactions in which* $\mathbf{N}O_2Ho$ *is reduced entirely and is converted into ammonia,* $\mathbf{N}H_3$.

All nitrates when fused with KHo, $\mathbf{Ca}Ho_2$ or soda-lime and some non-nitrogenous organic substance, such as sugar or starch, evolve ammonia, thus:—

$$3\mathbf{N}O_2Ko + 9KHo + \underset{\text{Sugar.}}{\mathbf{C}_6H_{12}O_6} = 6\mathbf{C}OKo_2 + 3\mathbf{N}H_3 + 6\mathbf{O}H_2.$$

The gas may be readily recognized by its odour, or action upon red litmus paper.

Nascent hydrogen, produced by the action of KHo upon metallic zinc, iron, or aluminium, gives rise, in the presence of a nitrate, to the formation of $\mathbf{N}H_3$, thus:—

$$\begin{aligned}&(1)\ Zn &&+ 2KHo = \mathbf{Zn}Ko_2 + H_2.\\ &(2)\ \mathbf{N}O_2Ko &&+ 4H_2 \ \ = \mathbf{N}H_3 \ \ + KHo + 2\mathbf{O}H_2.\end{aligned}$$

When $\mathbf{Sn}Cl_2$, HCl, and a nitrate are heated together, the tendency of the stannous chloride to combine with two more atoms of chlorine to form stannic chloride, aided by the oxidizing action of nitric acid upon the hydrogen, breaks up HCl, with formation of $\mathbf{Sn}Cl_4$ and $\mathbf{N}H_3$, thus:—

$$4\mathbf{Sn}Cl_2 + \mathbf{N}O_2Ko + 10HCl = 4\mathbf{Sn}Cl_4 + \mathbf{N}H_4Cl + KCl + 3\mathbf{O}H_2.$$

To detect *free* nitric acid in the presence of a nitrate, evaporate the solution on a water-bath with quill cuttings or white woollen fabrics. Nitric acid colours these substances yellow. Or digest the solution at a gentle heat with $\mathbf{C}OBao''$, filter off and test the filtrate by means of sulphuric acid and ferrous sulphate.

QUESTIONS AND EXERCISES.

1. How is nitric acid obtained, and what are its characteristic properties?
2. Explain what changes take place when nitrates are heated by themselves.
3. Explain the action of *aqua regia* upon metallic tin and antimony.
4. State what action takes place when ferrous, cuprous, and mercurous chlorides are heated with nitric acid.
5. Why can the metals Cu, Pb, Ag, be employed for the detection of nitric acid or a nitrate?
6. Explain what changes take place when a solution of potassic nitrate, potassic iodide, starch, and dilute sulphuric acid are mixed together.
7. What is the action of concentrated nitric acid upon the metals Fe, Sn, Sb, Pt?
8. How can ammonia be obtained from a nitrate? Describe several processes.
9. How would you test for nitrates in a soil, in sewage water, in mineral waters?
10. How much ferrous sulphate ($\mathbf{S}OHo_2Feo'' + 6aq.$) is required for the complete decomposition of 1 grm. of pure potassic nitrate?
11. Calculate how much nitre is required to deflagrate, 1st, 1·5 grm. of sugar, and 2nd, ·5 grm. of sulphur.
12. How is free nitric acid detected in the presence of a nitrate?

NITROUS ACID, $\mathbf{N}OHo$.—Obtained by the decomposition of $\mathbf{N}_2O_4$ in the presence of water (comp. Chapter XIV.) according to the equation:—

$$\mathbf{N}_2O_4 + \mathbf{O}H_2 = \mathbf{N}O_2Ho + \mathbf{N}OHo.$$

Its solution is prone to decompose into $\mathbf{N}O_2Ho$ and $\mathbf{N}_2O_2$ according to the equation:—

$$3\mathbf{N}OHo = \mathbf{N}O_2Ho + \mathbf{N}_2O_2 + \mathbf{O}H_2.$$

Nitrous anhydride is decomposed by water into $\mathbf{N}O_2Ho$ and $\mathbf{N}_2O_2$, thus:—

$$3\mathbf{N}_2O_3 + \mathbf{O}H_2 = 2\mathbf{N}O_2Ho + 2\mathbf{N}_2O_2.$$

REACTIONS IN THE DRY WAY.

Nitrites fuse and are decomposed on ignition into oxides, with evolution of nitrogen and oxygen. Ammonic nitrite ($\mathbf{N}OAmo$) breaks up, when heated, into nitrogen and water. Mixed with carbon, potassic cyanide, sulphur and other oxidizable bodies, nitrites deflagrate like nitrates, with which they have, in fact, most of the dry reactions in common.

REACTIONS IN THE WET WAY.

All nitrites are soluble in water; argentic nitrite, $\mathbf{N}OAgo$, is difficultly soluble, and serves for the preparation of pure nitrites, by double decomposition with neutral chlorides. Dilute acids ($\mathbf{S}O_2Ho_2$ or HCl) liberate $\mathbf{N}_2O_2$ and convert a portion of the nitrite into nitrate, thus:—

$$3\mathbf{N}OKo + \mathbf{S}O_2Ho_2 = \mathbf{N}_2O_2 + \mathbf{N}O_2Ko + \mathbf{S}O_2Ko_2 + \mathbf{O}H_2.$$

The reactions by which the presence of nitrous acid can be readily recognized, may be divided into two classes:—

1st. *Reactions in which the acid acts as an oxidizing agent:—*

$\mathbf{S}H_2$ decomposes aqueous solutions of alkaline nitrites, with formation of $\mathbf{N}_2O_2$ (of $\mathbf{N}H_3$ when the reaction goes on for some time) and alkaline sulphides, thus:—

$$2\mathbf{N}OKo + 2\mathbf{S}H_2 = \mathbf{N}_2O_2 + 2\mathbf{O}H_2 + \mathbf{S}_2K_2.$$

In acid solutions the decomposition is accompanied by a copious separation of sulphur.

$\mathbf{Fe}Cl_2$, on the addition of a little hydrochloric acid, is turned dark brown, if $\mathbf{N}OHo$ is present, owing to the absorption of $\mathbf{N}_2O_2$ gas by a portion of the unoxidized ferrous salt. On the application of heat $\mathbf{N}_2O_2$ is evolved, thus:—

$$2\mathbf{Fe}Cl_2 + 4HCl + 2\mathbf{N}OKo = \mathbf{Fe}_2Cl_6 + 2KCl + \mathbf{N}_2O_2 + 2\mathbf{O}H_2.$$

$\mathbf{N}O(NH_4O)$ breaks up into N and $\mathbf{O}H_2$, the hydrogen of the $\mathbf{N}H_4$ acting as the reducing agent. Nitrites containing fixed bases are decomposed in like manner, on the addition of ammonic chloride (or some other ammonic salt), and on heating, thus:—

$$\mathbf{C}OAmo_2 + 2\mathbf{N}OKo = N_4 + 4\mathbf{O}H_2 + \mathbf{C}OKo_2.$$

KI and starch solution give in the presence of a nitrite and a dilute acid blue iodide of starch. (See under HI, p. 256).

2nd. *Reactions in which the acid acts as a reducing agent, and is converted into nitric acid*, thus:—

$$2\mathbf{N}OHo + O_2 = 2\mathbf{N}O_2Ho.$$

$\mathbf{Au}Cl_3$ and $\mathbf{Hg}_2Cl_2$ give metallic gold and grey metallic mercury.

$\left\{\begin{matrix}\mathbf{Mn}O_2\ (OKo) \\ \mathbf{Mn}O_2\ (OKo)\end{matrix}\right\}$ oxidizes nitrites into nitrates, and a permanganate solution is rapidly decolorized, in the presence of a mineral acid ($\mathbf{S}O_2Ho_2$, HCl).

$\left\{\begin{matrix}\mathbf{Cr}O_2Ko \\ O \\ \mathbf{Cr}O_2Ko\end{matrix}\right.$ is reduced under similar conditions to a chromic salt.

Nitrates are not affected by potassic permanganate or alkaline chromates.

$\mathbf{Pb}O_2$ converts $\mathbf{N}OHo$ into $\mathbf{N}O_2Ho$; but does not act upon dilute $\mathbf{N}O_2Ho$ (DISTINCTION BETWEEN NITROUS AND NITRIC ACID).

QUESTIONS AND EXERCISES.

1. Explain the changes which take place when $\mathbf{N}_2O_4$ is acted upon by KHo.
2. Explain what takes place when nitrites are heated, 1st, by themselves; 2nd, in contact with carbon or sulphur.
3. How can $\mathbf{N}OKo$ be separated from $\mathbf{N}O_2Ko$?
4. What is the action of dilute sulphuric acid upon $\mathbf{N}OKo$?
5. Give instances, 1st, of the oxidizing, and 2nd, of the reducing action of $\mathbf{N}OHo$; and express the changes by equations.
6. What are the products of decomposition of strongly ignited $\mathbf{N}_2O_4Pbo''$, $\mathbf{N}O(NH_4O)$, and $\mathbf{N}OKo$?
7. How can a trace of a nitrite be detected in the presence of a nitrate?
8. Explain the action of concentrated $\mathbf{N}O_2Ho$, 1st, upon starch, 2nd, upon $\mathbf{As}_2O_3$.
9. How would you prepare pure $\begin{matrix}\mathbf{N}O \\ \mathbf{N}O\end{matrix}Cao''$?
10. Explain the action of heat upon a solution of $\begin{matrix}\mathbf{N}O \\ \mathbf{N}O\end{matrix}Cao''$ and AmCl.

HYDROCHLORIC ACID, HCl.—This compound has already been described (page 68) as a colourless gas, which is readily absorbed by water, and forms one of the most important acids. *Chlorides* are among the most important chemical compounds. They differ considerably in their physical properties.

REACTIONS IN THE DRY WAY.

Some chlorides are liquid and can be distilled without decomposition, such as $\mathbf{Sb}Cl_3$, $\mathbf{Sn}Cl_4$; others are solid, fusible and non-volatile, such as AgCl, $\mathbf{Pb}Cl_2$, $\mathbf{Ba}Cl_2$, NaCl. Upon ignition certain chlorides, such as $\mathbf{Au}Cl_3$, $\mathbf{Pt}Cl_4$, are decomposed with evolution of chlorine gas, first into $\mathbf{Au}Cl$, and $\mathbf{Pt}Cl_2$, which are almost insoluble in water, and finally into Au and Pt. Magnesic chloride is decomposed in the presence of water into $\mathbf{Mg}O$ and $2HCl$. Anhydrous ferric chloride, when heated in contact with air, is decomposed into $\mathbf{Fe}_2O_3$ and $3Cl_2$.

Heated in a bead of microcosmic salt, saturated with $\mathbf{Cu}O$, chlorides impart a *blue* color to the *outer flame*, owing to the formation of volatile $\mathbf{Cu}Cl_2$.

When a *dry* chloride is mixed with dipotassic dichromate and concentrated sulphuric acid, and gently heated in a small retort, a *deep brownish red* gas, called **chlorochromic acid,** $\mathbf{Cr}O_2Cl_2$, comes off, which condenses to a like coloured liquid and can be collected in a receiver. The reaction which takes place is expressed by the equation:—

$$4NaCl + \mathbf{Cr}_2O_5Ko_2 + 3\mathbf{S}O_2Ho_2 = \underset{\text{Chlorochromic acid.}}{2\mathbf{Cr}O_2Cl_2} + 2\mathbf{S}O_2Nao_2$$

$$+ \mathbf{S}O_2Ko_2 + 3\mathbf{O}H_2.$$

This liquid is speedily decomposed, on dilution with water, into chromic and hydrochloric acids, thus:—

$$\mathbf{Cr}O_2Cl_2 + 2\mathbf{O}H_2 = \mathbf{Cr}O_2Ho_2 + 2HCl;$$

or by ammonia or potassic hydrate into the corresponding salts. The presence of chromic acid and indirectly of hydrochloric acid is inferred from the yellow precipitate which a plumbic salt produces with their solutions. This reaction is employed *for recognizing chlorides in the presence of bromides.* The latter yield bromine when treated similarly.

REACTIONS IN THE WET WAY.

A SOLUTION OF SODIC CHLORIDE is employed.

All Chlorides may be divided into:—

1st. *Chlorides insoluble in water*, such as $AgCl$ and $\mathbf{Hg}_2Cl_2$, which are quite insoluble; $\mathbf{Pb}Cl_2$ which is difficultly soluble in cold, readily soluble in boiling water; and $\mathbf{Cu}_2Cl_2$, $\mathbf{Au}Cl$ and $\mathbf{Pt}Cl_2$, which are almost insoluble in water.

2nd. *Chlorides which are soluble in water*, comprising all other chlorides.

In order to ascertain the presence of a soluble chloride or of hydrochloric acid, we have merely to add a soluble argentic, mercurous or plumbic salt, when a white precipitate is produced. The first of these salts answers every purpose, and is therefore invariably used to detect hydrochloric acid.

$\mathbf{N}O_2Ago$ gives a *white curdy* precipitate of **argentic chloride,** $AgCl$, especially from a solution acidulated with nitric acid. The precipitate turns *violet* on exposure to light. It is insoluble in dilute nitric acid; soluble in ammonic hydrate, but is reprecipitated unchanged, on the addition of nitric acid; it is likewise soluble in potassic cyanide and sodic hyposulphite; soluble to a considerable extent in alkaline chlorides, from which $AgCl$ is reprecipitated on dilution.

Chlorides are detected also by heating with a little black manganic oxide and concentrated sulphuric acid, when chlorine is evolved according to the equation:—

$$\mathbf{Mn}O_2 + 2NaCl + 2\mathbf{S}O_2Ho_2 = Cl_2 + \mathbf{S}O_2Mno'' + \mathbf{S}O_2Nao_2 + 2\mathbf{O}H_2.$$

a gas which has been already described (Chapter VIII, Part I) and which is readily recognized by its characteristic odour and bleaching properties, its yellowish green colour, and its action upon iodized starch paper, or upon a dilute solution of potassic iodide and freshly prepared starch, giving rise to the formation of blue iodide of starch.

Concentrated sulphuric acid liberates gaseous hydrochloric acid from chlorides, thus:—

$$2NaCl + \mathbf{S}O_2Ho_2 = \mathbf{S}O_2Nao_2 + 2HCl.$$

$\mathbf{Hg}Cl_2$, $\mathbf{Hg}_2Cl_2$, $AgCl$, $\mathbf{Pb}Cl_2$, $\mathbf{Sn}Cl_2$, and $\mathbf{Sn}Cl_4$, are decomposed, with difficulty only, or not at all, by concentrated sulphuric acid.

In order to effect the decomposition of insoluble chlorides, such as $AgCl$, $\mathbf{Hg}_2Cl_2$, and $\mathbf{Pb}Cl_2$, they are fused in a porcelain crucible mixed with fusion mixture perfectly free from alkaline chlorides. The chlorine is transferred to the alkali metals, and may be readily detected by means of $\mathbf{N}O_2Ago$ in the aqueous extract, after acidulating with dilute nitric acid.

Traces of *free* HCl, in the presence of a soluble chloride, are best detected by gently heating with $\mathbf{Mn}O_2$ or $\mathbf{Pb}O_2$, and passing the evolved chlorine into a solution of potassic iodide and starch. The chlorine liberates iodine ($2KI + Cl_2 = 2KCl + I_2$) which forms with the starch blue iodide of starch.

QUESTIONS AND EXERCISES.

1. State how you would prepare dry hydrochloric acid gas.
2. How are the several solid chlorides acted upon by heat?
3. How is chlorochromic acid prepared?
4. Classify all chlorides according to their solubility in water.
5. Describe the most characteristic tests for chlorine and for hydrochloric acid or chlorides.
6. How are insoluble chlorides examined?
7. How would you detect free HCl in the presence of a metallic chloride?
8. Explain the action of distilled water, of chlorine water, ammonic hydrate, potassic cyanide, sodic hyposulphite, and sulphuric acid upon $AgCl$, $\mathbf{Hg}_2Cl_2$, and $\mathbf{Pb}Cl_2$.
9. You have given to you 100 c.c. of a liquid containing free HCl and a solution of sodic chloride. 50 c.c. of the liquid gave 2·345 grms. of AgCl. After evaporation and ignition of the other 50 c.c. the residue yielded 1·596 grm. of AgCl. What is the percentage of HCl and of sodic chloride in the liquid?

CHLORIC ACID, $\left\{\begin{matrix}\mathbf{O}\mathrm{Cl}\\ \mathbf{O}\mathrm{Ho}\end{matrix}\right.$.—Obtained, in combination with calcium, by passing chlorine through a solution of calcic hydrate and potassic carbonate to complete saturation. To a concentrated solution of the calcic chlorate, formed according to the equation:—

$$6\mathbf{Ca}\mathrm{Ho}_2 + 6\mathrm{Cl}_2 = \left\{\begin{matrix}\mathbf{O}\mathrm{Cl}\\ \mathbf{O}\\ \mathrm{Cao}''\\ \mathbf{O}\\ \mathbf{O}\mathrm{Cl}\end{matrix}\right. + 5\mathbf{Ca}\mathrm{Cl}_2 + 6\mathbf{O}\mathrm{H}_2,$$

add a solution of potassic chloride, when calcic chloride and potassic chlorate, $\left\{\begin{matrix}\mathbf{O}\mathrm{Cl}\\ \mathbf{O}\mathrm{Ko}\end{matrix}\right.$, are formed by double decomposition. Potassic chlorate, being little soluble in cold water, and still less so in a solution of $\mathbf{Ca}\mathrm{Cl}_2$, crystallises out, and is washed with cold water and purified by recrystallisation.

REACTIONS IN THE DRY WAY.

All chlorates are decomposed by heat; they fuse and evolve oxygen, or a mixture of chlorine and oxygen, according to the greater or less affinity of the metal for oxygen or chlorine, leaving a residue, consisting of a metallic chloride, oxychloride, or oxide.

On heating a few crystals of potassic chlorate in a test-tube, the presence of oxygen can be shown by introducing a glowing splinter of wood into the test-tube. On dissolving the fused mass in water, and adding a drop of $\mathbf{N}\mathrm{O}_2\mathrm{Ago}$, a white curdy precipitate is obtained, whilst before ignition the chlorate solution gave no precipitate.

Chlorates part with their oxygen far more readily, upon ignition, than nitrates. When mixed with oxidizable substances, such as C, S, P, or KCy, they explode violently, even when gently rubbed together in a mortar, or when moistened with a drop of concentrated sulphuric acid. Care should, therefore, be taken to powder, or heat together, only very small quantities of a chlorate and organic substances.

REACTIONS IN THE WET WAY.

A SOLUTION OF POTASSIC CHLORATE may be employed.

All chlorates are soluble in water. In order, therefore, to detect a chlorate, we avail ourselves of its powerful oxidizing action, and its leaving for the most part a chloride on ignition. Hydrochloric and strong sulphuric acids decompose chlorates, with evolution of chlorine and formation of lower oxides of chlorine.

Concentrated $\mathbf{S}\mathrm{O}_2\mathrm{Ho}_2$ decomposes potassic chlorate even in the cold, a *greenish yellow gas*, called **chloric peroxide**, $\mathbf{O}_4\mathrm{Cl}_2$, comes off, which is recognized by its suffocating odour. On the application of heat (especially on operating with somewhat large quantities) violent explosions occur. A few crystals only of the chlorate should, therefore, be employed, and the test-tube should be held with its mouth turned away from the operator. The change may be expressed by the equation:—

$$3\left\{\begin{matrix}\mathbf{O}\mathrm{Cl}\\ \mathbf{O}\mathrm{Ko}\end{matrix}\right. + \mathbf{S}\mathrm{O_2Ho_2} = \mathbf{S}\mathrm{O_2HoKo} + \underset{\substack{\text{Potassic}\\ \text{perchlorate.}}}{\left\{\begin{matrix}\mathbf{O}\mathrm{Cl}\\ \mathrm{O}\\ \mathbf{O}\mathrm{Ko}\end{matrix}\right.} + \underset{\substack{\text{Chloric}\\ \text{peroxide.}}}{\left\{\begin{matrix}\mathbf{O}\mathrm{Cl}\\ \mathrm{O_2}\\ \mathbf{O}\mathrm{Cl}\end{matrix}\right.} + \mathbf{O}\mathrm{H_2}.$$

HCl, especially when heated, decomposes potassic chlorate, giving off a mixture of chloric peroxide and free chlorine, called *euchlorine*, thus:—

$$8\left\{\begin{matrix}\mathbf{O}\mathrm{Cl}\\ \mathbf{O}\mathrm{Ko}\end{matrix}\right. + 24\mathrm{HCl} = 3\left\{\begin{matrix}\mathbf{O}\mathrm{Cl}\\ \mathrm{O_2}\\ \mathbf{O}\mathrm{Cl}\end{matrix}\right. + 9\mathrm{Cl_2} + 8\mathrm{KCl} + 12\mathbf{O}\mathrm{H_2}.$$

A solution of indigo (sulphindigotic acid) is decolorized on the addition of a solution of a chlorate and a little sulphuric acid, by a reaction analogous to that produced by free nitric acid.

In order *to distinguish a nitrate from a chlorate*, dissolve a small portion of the two salts in water, and add a few drops of argentic nitrate to make sure that no chloride is present. Ignite another portion strongly till the evolution of oxygen ceases; allow to cool, and dissolve out with hot water. To one portion of the solution add a few drops of dilute nitric acid, and then argentic nitrate. A white curdy precipitate indicates the presence of a chloride, and, indirectly, of a chlorate. To the other portion of the solution add potassic iodide and starch solution, and then a few drops of acetic acid; a blue coloration of iodide of starch proves the presence of a nitrite, derived from the potassic nitrate.

If a *chloride be present, as well as a chlorate and nitrate*, $\mathbf{S}\mathrm{O_2Ago_2}$ must be added to the solution, as long as a precipitate comes down. The AgCl is filtered off, and the filtrate evaporated to dryness, with the addition of a little pure sodic carbonate, and the residue strongly ignited. The dry mass is extracted with a little boiling water, filtered, and argentic nitrate added to a portion of the acidulated ($\mathbf{N}\mathrm{O_2Ho}$) solution, as long as a precipitate comes down. The remaining portion is tested for nitric acid, either by the iodide of starch reaction, or by means of a ferrous salt and sulphuric acid.

QUESTIONS AND EXERCISES.

1. State briefly how potassic chlorate is prepared.
2. Describe the changes which potassic chlorate undergoes on ignition.
3. Explain the action—1st, of concentrated sulphuric acid; 2nd, of concentrated hydrochloric acid upon potassic chlorate. Give equations.
4. How can a chlorate be detected in the presence of a chloride?
5. How can a nitrate and a chloride be recognized in the presence of a chlorate?
6. How much oxygen, by weight and by volume, can be obtained from 100 grms. of potassic chlorate?
7. Introduce some strips of metallic copper into a mixture of potassic chlorate, arsenious acid and hydrochloric acid, and explain why no precipitate of metallic arsenic is obtained on the copper.

HYPOCHLOROUS ACID, ClHo.—The salts which this acid forms possess considerable interest, on account of the powerful bleaching action which they exert in the presence of acids. Of importance are the sodic and calcic hypochlorites, which are obtained along with the corresponding chlorides, by passing chlorine through a solution of the carbonates or hydrates. An important compound closely related to the hypochlorites is the calcic chlorohypochlorite, commonly called chloride of lime or *bleaching powder*, which appears to be formed according to the equation :—

$$\mathbf{Ca}Ho_2 + Cl_2 = \mathbf{Ca}(OCl)Cl + \mathbf{O}H_2.$$

Hypochlorites are gradually decomposed on exposure to air (owing probably to the action of the carbonic anhydride contained in air). Dilute acids liberate chlorine, and it is on this account that hypochlorites are of such great value as ***disinfectants*** and ***bleaching agents.***

REACTIONS IN THE DRY WAY.

Hypochlorites are converted into chlorates (which give off oxygen when ignited), and chlorides, thus:—

$$6\mathbf{Ca}(OCl)Cl = \left\{\begin{array}{l}\mathbf{O}Cl\\ \begin{matrix}O\\O\end{matrix}Cao''\\ \mathbf{O}Cl\end{array}\right. + 5\mathbf{Ca}Cl_2.$$

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF CALCIC OR SODIC HYPOCHLORITE, ClNao.

All hypochlorites are soluble in water. Their aqueous solutions bleach vegetable colours. On heating or evaporating dilute solutions of hypochlorites, they are decomposed into chlorides and chlorates, concentrated solutions into chlorides and oxygen. Even weak acids decompose them with evolution of chlorine. (DISTINCTION BETWEEN HYPOCHLORITES AND CHLORATES.) Hypochlorites yield oxygen to readily oxidizable substances, and become converted into chlorides; the detection of hypochlorous acid is based upon the various processes of oxidation to which its salts can give rise, thus:—

$$\begin{array}{lccl}
\mathbf{As}_2O_3 & \text{is oxidized to} & & \mathbf{As}_2O_5.\\
\mathbf{Mn}Cl_2 & \text{,,} & \text{,,} & \mathbf{Mn}O_2.\\
\mathbf{Pb}O & \text{,,} & \text{,,} & \mathbf{Pb}O_2.\\
\mathbf{Pb}S & \text{,,} & \text{,,} & \mathbf{S}O_2Pbo''.\\
\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}OHo\end{array}\right. & \text{,,} & \text{,,} & 2\mathbf{C}O_2 + \mathbf{O}H_2.
\end{array}$$

Indigo or litmus solutions are readily decolorized.

QUESTIONS AND EXERCISES.

1. Give the graphic formula for *bleaching powder.*
2. Give illustrations of the oxidizing action of hypochlorites. Express the changes by equations.
3. How is calcic hypochlorite prepared?
4. Explain the bleaching action of an aqueous solution of a hypochlorite.
5. What change takes place—1st, when a hypochlorite is ignited by itself; 2ndly, when a concentrated solution of a hypochlorite is boiled?

6. Explain the deodorizing action of hypochlorites when brought in contact with $\mathbf{S}H_2$, $\mathbf{S}Am_2$, $\mathbf{P}H_3$, $\mathbf{N}H_3$.
7. How can a hypochlorite be distinguished in the presence of a chloride?
8. A sample of *bleaching powder* contains 26·5 per cent. of chlorine. How much $\mathbf{As}_2O_3$ by weight will be required to deoxidize 1·235 grm. of the bleaching powder?

HYDROBROMIC ACID, HBr.—The element bromine occurs in nature mainly in combination with the fixed alkalies and alkaline earthy metals (calcium, magnesium), forming salts, called bromides, which resemble the chlorides of the same metals very closely, and from which we derive both bromine and hydrobromic acid.

REACTIONS IN THE DRY WAY.

Most bromides remain unaltered when ignited; others are volatile without decomposition. $\mathbf{Au}Br_3$ and $\mathbf{Pt}Br_4$ are decomposed upon ignition into metal and bromine, which latter volatilizes. Many bromides are acted upon, when ignited with free access of air, and are converted into oxides and free bromine; others again, such as $\mathbf{Al}_2Br_6$, etc., are decomposed, on evaporation of their aqueous solutions, into oxides and hydrobromic acid. KBr and $NaBr$ are converted, to a great extent, into KCl and $NaCl$, on repeated ignition with ammonic chloride. When fused with hydric potassic sulphate, bromides are decomposed into sulphates, with evolution of sulphurous anhydride and bromine. The few insoluble bromides of the heavy metals are converted into soluble alkaline bromides by fusion with alkaline carbonates.

Heated before the blowpipe on a bead of microcosmic salt, in which a little cupric oxide has been diffused, bromides impart a *blue* colour to the flame, which passes into *green*, especially at the edges. This distinction between chlorides and bromides is, however, not very marked.

REACTIONS IN THE WET WAY.

A SOLUTION OF POTASSIC BROMIDE, KBr, may be employed.

All metallic bromides can be divided into—

1st. *Bromides which are insoluble in water*, such as $AgBr$, $'\mathbf{Hg}'_2Br_2$, $\mathbf{Pb}Br_2$ (less soluble in water than $\mathbf{Pb}Cl_2$), and—

2nd. *Bromides which are soluble in water*, comprising all other bromides.

Certain bromides, *e.g.*, $\mathbf{Sb}Br_3$, $\mathbf{Bi}Br_3$, are decomposed by water into insoluble oxybromides and hydrobromic acid. They resemble in this respect the corresponding chlorides.

In order to detect hydrobromic acid or a soluble bromide, add a solution of an argentic (mercurous or plumbic) salt to the solution, when a *yellowish white* precipitate of **argentic bromide**, $AgBr$, is formed, which is insoluble in dilute nitric acid, soluble only in concentrated ammonic hydrate, readily soluble in potassic cyanide or sodic hyposulphite. By decanting the supernatant liquid, washing with a little water, and treating the precipitated argentic bromide with strong hydrochloric acid, reddish brown fumes of bromine are evolved which colour starch paste *yellowish.* (DISTINCTION BETWEEN AgBr AND AgCl.)

Insoluble bromides, such as AgBr, $\mathbf{Hg}_2Br_2$, $\mathbf{Pb}Br_2$, can be decomposed by heating in a test-tube with alkaline carbonates (free from chlorides). The aqueous extract is tested for hydrobromic acid, and the insoluble residue for silver or lead. $\mathbf{Hg}_2Br_2$ gives a sublimate of metallic mercury.

In the absence of any well-marked distinguishing features in the argentic bromide precipitate, it is preferable to liberate bromine from soluble bromides, and to cause the *reddish brown* vapour to act upon starch paste with formation of yellowish *bromide of starch.*

Nitrous acid (or a nitrite and dilute hydrochloric acid) does not liberate any bromine from soluble bromides. (DISTINCTION BETWEEN BROMIDES AND IODIDES.) All bromides are, however, decomposed by chlorine, with evolution of bromine, which remains dissolved in the aqueous solution. On shaking with a little ether, the bromine is taken up by the ether, forming a yellowish red liquid, which floats on the top of the saline aqueous solution. This etherial liquid may be removed by means of a small pipette, and on being treated with potassic hydrate is converted, on evaporation, into potassic bromide and potassic bromate, $\left\{\begin{matrix}\mathbf{O}Br\\ \mathbf{O}Ko\end{matrix}\right.$, thus:—

$$3Br_2 + 6KHo = 5KBr + \left\{\begin{matrix}\mathbf{O}Br\\ \mathbf{O}Ko\end{matrix}\right. + 3\mathbf{O}H_2.$$

Bromine is obtained from natural bromides, such as KBr, $\mathbf{Mg}Br_2$, $\mathbf{Ca}Br_2$, by reactions analogous to those employed for the preparation of chlorine from common salt (page 247), for instance, on distilling with manganic oxide and concentrated sulphuric acid, thus:—

$$2KBr + \mathbf{Mn}O_2 + 2\mathbf{S}O_2Ho_2 = Br_2 + \mathbf{S}O_2Ko_2 + \mathbf{S}O_2Mno'' + 2\mathbf{O}H_2,$$

or by distilling a bromide with dipotassic dichromate and sulphuric acid, thus:—

$$6KBr + \mathbf{Cr}_2O_5Ko_2 + 7\mathbf{S}O_2Ho_2 = 3Br_2 + \mathbf{S}_3O_6Cr_2o^{vi} + 4\mathbf{S}O_2Ko_2 + 7\mathbf{O}H_2.$$

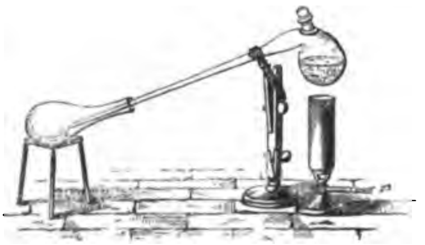


FIG. 85.

A mixture of a bromide and $\mathbf{Mn}O_2$ or $\mathbf{Cr}_2O_5Ko_2$ is introduced into a tubulated retort (Fig. 85) with concentrated sulphuric acid, diluted with its own weight of water, and gently heated over a gas flame, or in a small water-bath. The vapour of bromine passes over, and condenses in a flask (which should be kept cold by a stream of water, or, better still, in a vessel surrounded with ice), to a reddish brown heavy liquid.

Concentrated $\mathbf{S}O_2Ho_2$ alone evolves HBr, together with bromine and $\mathbf{S}O_2$, thus:—

$$4KBr + 3\mathbf{S}O_2Ho_2 = Br_2 + 2HBr + 2\mathbf{S}O_2Ko_2 + 2\mathbf{O}H_2 + \mathbf{S}O_2.$$

Concentrated $\mathbf{N}O_2Ho$ evolves bromine, together with nitrous fumes, thus:—

$$2KBr + 4\mathbf{N}O_2Ho = Br_2 + 2\mathbf{N}O_2Ko + \mathbf{N}_2O_4 + 2\mathbf{O}H_2.$$

In the two last reactions the sulphuric and nitric acids act as oxidizing agents, performing in fact the functions of the $\mathbf{Mn}O_2$ and $\mathbf{Cr}_2O_5Ko_2$ in the former reactions.

It is obvious that the hydrogen may also be removed from hydrobromic acid (or the metal from a metallic bromide) by other oxidizing agents, such as permanganates and metallic peroxides, in the presence of an acid.

Bromine is a heavy reddish brown liquid, of disagreeable odour, resembling the odour of chlorine. It boils at 63° C., and volatilizes at the ordinary temperature. Bromine vapour bleaches vegetable colours, like chlorine gas. It is difficultly soluble in water, somewhat more soluble in alcohol, and readily soluble in ether to a yellowish red liquid.

Bromine (like chlorine) is an oxidizing agent, *i.e.*, it is eager to combine with hydrogen, and is capable of decomposing $\mathbf{O}H_2$, $\mathbf{S}H_2$, etc., under favourable circumstances (*e.g.*, sunlight), with liberation of oxygen, sulphur, etc. We avail ourselves of this tendency to prepare hydrobromic acid, which cannot be obtained pure by distilling a bromide with sulphuric acid. By passing sulphuretted hydrogen through bromine suspended in water, a colourless solution of hydrobromic acid is obtained, and sulphur separates, thus:—

$$Br_2 + \mathbf{S}H_2 = 2HBr + S.$$

This solution always contains some sulphuric acid, owing to a secondary reaction of the bromine upon water, in the presence of nascent sulphur:—

$$3Br_2 + 4\mathbf{O}H_2 + S = 6HBr + \mathbf{S}O_2Ho_2,$$

from which the hydrobromic acid is separated by distillation.

It will be inferred from this that the decomposition of water by bromine would be assisted very much by the presence of deoxidising bodies, such as phosphorus, metallic hypophosphites, sulphites, hyposulphites.

Hydrobromic acid can likewise be prepared by distilling an alkaline bromide with phosphoric acid.

In order *to distinguish a bromide in the presence of a chloride*, argentic nitrate is added gradually to the solution, acidulated with a little dilute nitric acid.

AgBr is precipitated first, and by filtering off, as soon as the precipitate appears white—an indication that the whole of the bromide has been precipitated, and that AgCl begins to fall out—the two acids may be roughly separated.

It is, however, preferable to employ the reaction described at page 246, viz., of distilling a mixture of a dry chloride and bromide with dipotassic dichromate and concentrated sulphuric acid, and of obtaining chlorochromic acid and bromine, the former being decomposed by water into $\mathbf{Cr}O_2Ho_2$ and HCl. The bromine remaining unchanged, can be removed by ether. On adding AmHo to the bromine solution a colourless liquid of ammonic bromide and bromate is obtained.

QUESTIONS AND EXERCISES.

1. Describe several methods by which bromine can be obtained from soluble bromides.
2. How would you prepare HBr from a soluble bromide?
3. Explain the action of heat upon solid soluble bromides.
4. Classify all bromides according to their solubility in water.
5. Describe the most characteristic tests for bromine and for HBr.
6. Explain the action of chlorine, dilute HCl, concentrated $\mathbf{S}O_2Ho_2$, concentrated $\mathbf{N}O_2Ho$, and $\mathbf{P}OHo_3$ upon potassic bromide.
7. How is HBr distinguished from HCl?
8. What takes place when bromine, phosphorus, and water are brought together?
9. Explain the action of $\mathbf{S}H_2$, $\mathbf{S}ONao_2$, and $\mathbf{S}SONao_2$ upon bromine suspended in water.
10. Give the atomic and volume weights of bromine and of hydrobromic acid.
11. 1·56 grm. of argentic bromide are heated in a current of chlorine; what will be the weight of the silver salt left?

BROMIC ACID, $\left\{\begin{matrix}\mathbf{O}Br\\ \mathbf{O}Ho\end{matrix}\right.$.—Obtained in combination with potassium by adding bromine to a moderately concentrated solution of potassic hydrate. Potassic bromate, $\left\{\begin{matrix}\mathbf{O}Br\\ \mathbf{O}Ko,\end{matrix}\right.$ crystallises out from the slightly yellowish coloured liquid, and is purified from potassic bromide by washing with water and recrystallisation. The reaction takes place according to the equation:—

$$3Br_2 + 6KHo = 5KBr + \left\{\begin{matrix}\mathbf{O}Br\\ \mathbf{O}Ko\end{matrix}\right. + 3\mathbf{O}H_2.$$

The free acid is obtained by decomposing baric bromate with dilute sulphuric acid.

REACTIONS IN THE DRY WAY.

All bromates are decomposed by heat. Some, *e.g.*, the alkaline bromates, fuse and evolve oxygen, leaving a bromide; others, such as zincic and magnesic bromates, leave an oxide and give off oxygen and bromine; others, again, leave an oxide and a bromide, *e.g.*, plumbic and cupric bromates. When mixed with readily oxidizable substances, such as carbon, sulphur, etc., bromates deflagrate.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF POTASSIC BROMATE, $\left\{\begin{matrix}\mathbf{O}Br\\ \mathbf{O}Ko\end{matrix}\right.$.

All bromates are soluble in water. Argentic and mercurous bromates are difficultly soluble.

Dilute $\mathbf{S}O_2Ho_2$, $\mathbf{N}O_2Ho$, or $\mathbf{P}OHo_3$ liberates bromic acid from its salts, which, however, exhibits great instability and breaks up into bromine, oxygen, and water.

Bromates are readily broken up by deoxidizing substances, such as $\mathbf{S}O_2$, $\mathbf{P}_2O_3$, $\mathbf{S}H_2$, with formation of $\mathbf{S}O_2Ho_2$, $\mathbf{P}OHo_3$, sulphur and water, and liberation of bromine. A mixture of potassic bromide and bromate, when acted upon by dilute acids (HCl, $\mathbf{S}O_2Ho_2$), is decomposed into bromine and water, thus:—

$$5KBr + \left\{\begin{matrix}\mathbf{O}Br\\ \mathbf{O}Ko\end{matrix}\right. + 6HCl = 3Br_2 + 3\mathbf{O}H_2 + 6KCl.$$

The weak affinity of bromine for oxygen is, moreover, rendered apparent on boiling bromine with such powerful oxidizing agents as $\mathbf{N}O_2Ho$, $\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}Ko\end{matrix}\right.$, $\mathbf{Mn}_2O_6Ko_2$, which are without action upon it.

A bromate in the presence of a chlorate is readily distinguished by precipitation with $\mathbf{N}O_2Ago$; the *white* **argentic bromate,** $\left\{\begin{matrix}\mathbf{O}Br\\ \mathbf{O}Ago\end{matrix}\right.$, gives off bromine on being treated with HCl. The residue which bromates and chlorates leave on ignition may also be tested by any of the methods described under hydrochloric and hydrobromic acids.

QUESTIONS AND EXERCISES.

1. State how potassic and baric bromates are prepared.
2. Describe the changes which metallic bromates undergo when submitted to heat.
3. Explain the action of dilute acids upon potassic bromate.
4. What is the action of $\mathbf{S}H_2$, $\mathbf{S}O_2$, or $\mathbf{P}_2O_3$ upon potassic bromate?
5. How can a bromate be distinguished in the presence of a bromide?
6. How can a bromate be distinguished from a chlorate or nitrate?
7. How is free bromic acid obtained?
8. How much potassic bromate should there be obtained from 50 grms. of bromine?

HYDRIODIC ACID, HI.—Occurs in nature in the form of soluble iodides (KI, NaI, $\mathbf{Mg}I_2$, $\mathbf{Ca}I_2$), in sea water, in the ashes of marine plants, in some mineral springs, from which bodies iodine is obtained, by processes similar to those employed for the extraction of bromine from bromides.

REACTIONS IN THE DRY WAY.

Most iodides undergo decomposition when heated by themselves, either with or without exclusion of air. $\mathbf{Au}I_3$ and $\mathbf{Pt}I_4$ give off iodine, and leave the metals; others are partially decomposed, giving off iodine, and leaving an oxide of the metal. The alkaline iodides, however, can be heated to fusion, without undergoing any decomposition. Ignition with AmCl converts iodides only partially into chlorides. On fusing cupric oxide in a bead of microcosmic salt, and introducing a little potassic iodide into the bead and heating in the inner blowpipe flame, the outer flame becomes of a *fine emerald green colour.*

REACTIONS IN THE WET WAY.

We employ a SOLUTION OF POTASSIC IODIDE, KI.

All metallic iodides may be divided into—

1st. *Iodides insoluble in water*, such as AgI, $\mathbf{Hg}_2I_2$, $\mathbf{Hg}I_2$, $\mathbf{Pb}I_2$, $\mathbf{Cu}_2I_2$, and—

2nd. *Iodides soluble in water*, comprising all others. The iodides of the heavy metals are less soluble than the corresponding bromides or chlorides.

Soluble iodides may be examined in two ways—

1st. *By precipitation or conversion of the soluble into insoluble iodides.*

$\mathbf{N}O_2Ago$ gives a *yellowish white* precipitate of **argentic iodide**, AgI, insoluble in dilute nitric acid, almost entirely insoluble in ammonic hydrate (DISTINCTION BETWEEN HI AND HCl, or HBr); soluble in potassic cyanide.

$\mathbf{N}_2O_4Hg_2o''$ gives a *yellowish green* precipitate of **mercurous iodide**, $\mathbf{Hg}_2I_2$, insoluble in dilute nitric acid, soluble in potassic iodide.

$\mathbf{Hg}Cl_2$ gives a beautiful *vermilion red* precipitate of **mercuric iodide**, $\mathbf{Hg}I_2$, soluble, however, in excess either of mercuric chloride or of potassic iodide.

$\left(\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}O\end{matrix}\right.\right)_2Pbo''$ gives a *bright yellow* precipitate of **plumbic iodide**, $\mathbf{Pb}I_2$, soluble, like the chloride, in hot water, from which it crystallises out, on cooling, in beautiful shining yellow scales; soluble in dilute nitric acid.

$\mathbf{S}O_2Cu_2o''$ (**cuprous sulphate**), obtained by treating $\mathbf{S}O_2Cuo''$ with $\mathbf{S}OHo_2$, produce sa *dirty white* precipitate of **cuprous iodide**, $\mathbf{Cu}_2I_2$, which is of interest, because *chlorides and bromides cannot be precipitated in like manner*, and because it serves frequently for removing iodides from dilute solutions containing chlorides and bromides.

2nd. *By liberating iodine*, and causing the iodine vapour to act upon starch paste. This may be effected in several ways.

On mixing a dilute solution of potassic iodide with a few drops of hydrochloric acid, and then adding a drop or two of a solution of potassic nitrite, iodine is instantly liberated, and may be detected by the yellowish brown tint it imparts to the solution, or better still by allowing it to act upon a solution of starch, to which it imparts a *fine blue colour*, owing to the formation of *iodide of starch.* This is one of the most delicate tests. The reaction serves equally well for the detection of $\mathbf{N}OHo$ (comp. page 245), or $\mathbf{N}O_2Ho$, after reducing to $\mathbf{N}OHo$ (see page 242), thus:—

$$2KI + 2\mathbf{N}OKo + 4HCl = I_2 + 4KCl + \mathbf{N}_2O_2 + 2\mathbf{O}H_2.$$

A solution containing free iodine may also be shaken up with a few drops of carbonic disulphide, which dissolves the iodine, assuming a fine violet colour. Ether dissolves iodine, but the colour which is produced resembles ether coloured by bromine.

Nitric acid, containing a lower oxide of nitrogen, acts like a nitrite.

Bromine or chlorine (or what amounts to the same, ClNao and HCl, or metallic peroxides, *e.g.*, $\mathbf{Ba}O_2$, $\mathbf{Pb}O_2$, $\mathbf{Mn}O_2$, and HCl), liberates iodine from iodides. According to the quantity of iodide employed, iodine separates either as a bluish black powder, forming a brown liquid, or in the form of deep violet fumes, which condense to beautiful fern-leaf shaped crystals.

The methods adopted for the extraction of iodine from metallic iodides are all based upon the expulsion of iodine by oxygen (or its equivalent of chlorine or bromine). Iodine is obtained by distilling an iodide with an oxidizing agent and sulphuric acid, *e.g.*:—

$$2KI + \mathbf{Mn}O_2 + 2\mathbf{S}O_2Ho_2 = I_2 + \mathbf{S}O_2Mno'' + \mathbf{S}O_2Ko_2 + 2\mathbf{O}H_2, \text{ or}$$

$$6KI + \mathbf{Cr}_2O_6Ko_2 + 7\mathbf{S}O_2Ho_2 = 3I_2 + \mathbf{S}_3O_6Cr_2o^{vi} + 4\mathbf{S}O_2Ko_2 + 7\mathbf{O}H_2.$$

Concentrated acids, such as $\mathbf{S}O_2Ho_2$, or $\mathbf{N}O_2Ho$, decompose iodides with evolution of $\mathbf{S}O_2$ and lower oxides of nitrogen, thus:—

$$2KI + 2\mathbf{S}O_2Ho_2 = I_2 + \mathbf{S}O_2Ko_2 + \mathbf{S}O_2 + 2\mathbf{O}H_2.$$
$$2KI + 4\mathbf{N}O_2Ho = I_2 + 2\mathbf{N}O_2Ko + \mathbf{N}_2O_4 + 2\mathbf{O}H_2.$$

On fusing an iodide with $\mathbf{S}O_2HoKo$, iodine is likewise liberated, thus:—

$$2KI + 4\mathbf{S}O_2HoKo = 3\mathbf{S}O_2Ko_2 + \mathbf{S}O_2 + I_2 + 2\mathbf{O}H_2.$$

On examining for *traces* of iodine by acting upon an iodide with chlorine or bromine, excess of the latter elements must be carefully avoided, as the iodine forms with the chlorine or bromine colourless chloride or bromide of iodine, and destroys the blue colour of iodide of starch, or the violet colour of the carbonic disulphide solution. The blue colour of iodide of starch is also destroyed by various reducing agents, such as $\mathbf{S}O_2$, $\mathbf{S}H_2$, $\mathbf{As}_2O_3$, $\mathbf{Sn}Cl_2$, and $\mathbf{Hg}_2Cl_2$, or by any organic reducing body. Alkalies destroy the colour, dilute acids (even acetic acid) restore it again. On heating iodide of starch the colour disappears, but reappears on cooling.

The destruction of the blue colour of iodide of starch by various reducing agents is due to the decomposition of water by the iodine, with formation of HI, the oxygen being transferred to the reducing agent, thus:—

$\mathbf{S}OHo_2$ (a dilute solution) $+ I_2 + \mathbf{O}H_2 = \mathbf{S}O_2Ho_2 + 2HI.$
$\mathbf{S}H_2 \quad + I_2 = 2HI \quad + S.$
$\mathbf{As}Ho_3 + I_2 + \mathbf{O}H_2 = 2HI + \mathbf{As}OHo_3.$

Hydriodic acid is prepared by acting upon iodine suspended in water (or dissolved in hydriodic acid), with a current of $\mathbf{S}H_2$. Sulphur separates and is removed by filtration, and the solution of hydriodic acid concentrated by distillation. Its aqueous solution absorbs oxygen from the air, water being formed and iodine liberated, which dissolves in the undecomposed hydriodic acid, and imparts a brown colour to the liquid.

Insoluble iodides have to be fused with alkaline carbonates. The aqueous extract is examined for iodine, and the residue for the metal.

QUESTIONS AND EXERCISES.

1. How would you extract iodine from $\mathbf{Mg}I_2$? Give several methods, and express the changes by equations.
2. Explain the action of heat upon solid iodides.
3. Classify all iodides according to their solubility in water.
4. Explain how you would distinguish HCl, HBr, and HI, when occurring in one and the same substance.
5. Explain the action of iodine vapour upon starch.
6. Why is it preferable to liberate iodine by means of $\mathbf{N}_2O_3$ instead of by bromine or chlorine?
7. How would you prepare a solution of hydriodic acid?
8. How much iodine can be obtained from 100 lbs. of NaI?
9. Give graphic formulæ for cuprous and mercurous iodides.
10. Explain how you would distinguish free iodine in the presence of an iodide.
11. What action takes place when a dilute solution of $\mathbf{S}O_2$ acts upon iodine, and how can iodine be made the measure for $\mathbf{S}O_2$ and *vice versâ*?
12. 10 litres of a mineral water yield ·184 grm. of AgI; how much iodine is there in 100,000 parts of the water?

IODIC ACID, $\left\{\begin{matrix}\mathbf{O}I \\ \mathbf{O}Ho\end{matrix}\right.$.—Potassic iodate is obtained, like the corresponding chlorate and bromate, by dissolving iodine in potassic hydrate. The iodate crystallises out first, being much less soluble than KI. The free acid can be prepared by decomposing baric iodate with sulphuric acid, thus:—

$$\left\{\begin{matrix}\mathbf{O}I \\ \mathbf{O} \\ \mathbf{O} \\ \mathbf{O}I\end{matrix}\right. Bao'' + \mathbf{S}O_2Ho_2 = 2\left\{\begin{matrix}\mathbf{O}I \\ \mathbf{O}Ho\end{matrix}\right. + \mathbf{S}O_2Bao''.$$

Iodic acid is also obtained by the action of strong boiling nitric acid upon iodine, or by passing chlorine through iodine suspended in water.

REACTIONS IN THE DRY WAY.

All iodates are decomposed upon ignition, some breaking up into an iodide, with evolution of oxygen; others into metallic oxides, iodine and oxygen being expelled. When heated with charcoal they explode less violently than chlorates or bromates.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF POTASSIC IODATE, $\left\{\begin{matrix}\mathbf{O}I\\ \mathbf{O}Ko\end{matrix}\right.$.

Alkaline iodates alone are soluble in water.

$\mathbf{Ba}Cl_2$ gives a *white* precipitate of **baric iodate**, soluble in nitric acid.

$\mathbf{N}O_2Ago$ produces a *white* crystalline precipitate of **argentic iodate**, sparingly soluble in nitric acid, readily soluble in ammonic hydrate (DISTINCTION FROM HI). On the addition of a reducing agent, *e.g.*, $\mathbf{S}OHo_2$, to the clear ammoniacal solution of argentic iodate, a precipitate of AgI is obtained, thus:—

$$\left\{\begin{matrix}\mathbf{O}I\\ \mathbf{O}Ago\end{matrix}\right. + 3\mathbf{S}OHo_2 = AgI + 3\mathbf{S}O_2Ho_2.$$

Potassic iodate is decomposed by $\mathbf{S}H_2$, with formation of potassic iodide and sulphuric acid, and precipitation of sulphur; by $\mathbf{S}OHo_2$, with separation of iodine, which (by the decomposition of water) is converted into hydriodic acid.

A mixture of an iodate and iodide is decomposed by weak acids (*e.g.*, acetic acid), with liberation of iodine. Traces of an iodate in potassic iodide can, therefore, be detected by means of the delicate iodide of starch reaction.

Iodates which give off iodine when they come in contact with various reducing agents, *e.g.*, $\mathbf{S}O_2$, $\mathbf{S}SONao_2$, $\mathbf{Sn}Cl_2$ differ, however, in a marked manner from bromates by remaining unacted upon by concentrated sulphuric acid, unless the action be assisted by deoxidizing agents, such as ferrous salts, etc. Instead of acquiring a less stable character by the interposition of the atoms of oxygen between the iodine and potassium, potassic iodate, and still more so *periodate* (obtained by passing chlorine through an alkaline solution of potassic iodate), are capable of resisting the action of sulphuric acid far more readily than potassic iodide. Periodates are, in fact, not reduced by the ordinary reducing agents by which iodic acid is reduced, except by $\mathbf{S}H_2$.

QUESTIONS AND EXERCISES.

1. How are potassic iodate and periodate obtained? Give equations.
2. Explain the changes which iodates and periodates undergo upon ignition.
3. How can iodides, iodates, and periodates be distinguished from each other?
4. Explain the change which takes place when potassic iodate is acted upon— 1st, by reducing agents, *e.g.*, $\mathbf{S}O_2$, $\mathbf{S}H_2$, $\mathbf{Fe}Cl_2$; 2ndly, by concentrated sulphuric acid.
5. A precipitate contains AgI and $\left\{\begin{matrix}\mathbf{O}I\\ \mathbf{O}Ago\end{matrix}\right.$. State how you would separate the two salts from each other.
6. Explain the action of HI upon a mixture of KI and $\left\{\begin{matrix}\mathbf{O}I\\ \mathbf{O}Ko\end{matrix}\right.$.

HYDROFLUORIC ACID, HF.—Occurs in nature in combination chiefly with calcium in the mineral called *fluorspar* (*Derbyshire spar*), $\mathbf{Ca}F_2$; also as double fluoride of aluminium and sodium in *cryolite*, $6NaF,\mathbf{Al}_2F_6$. It is, moreover, met with in certain *natural phosphates*, *e.g.*, *coprolite*, *wavellite*, and in a few *silicates*, *e.g.*, *topaz*, *mica*, *hornblende*.

REACTIONS IN THE DRY WAY.

Heated out of contact with the air, most fluorides remain unchanged. Volatile fluorides can be distilled; but when heated in a moist atmosphere, or if water be added, they are decomposed into oxides (oxyfluorides) and hydrofluoric acid. The changes which fluorides undergo in the dry way are of two kinds—

1st. *The fluoride gives off hydrofluoric acid gas, which corrodes glass.*—By heating a fluoride containing water in a piece of combustion tubing, open at both ends, before the blowpipe, the glass around the fluoride is attacked. The experiment may be carried out also by mixing a little microcosmic salt with the fluoride, and holding the tube in a slightly slanting position.

By heating a mixture of a fluoride with $\mathbf{S}O_2HoKo$ in a test-tube, HF is disengaged, thus:—

$$\mathbf{Ca}F_2 + 2\mathbf{S}O_2HoKo = \mathbf{S}O_2Cao'' + \mathbf{S}O_2Ko_2 + 2HF.$$

The gas corrodes the upper part of the tube on account of its action upon the $\mathbf{Si}O_2$ of the glass, with which it forms a gaseous compound, silicic fluoride, $\mathbf{Si}F_4$, thus:—

$$4HF + \mathbf{Si}O_2 = \mathbf{Si}F_4 + 2\mathbf{O}H_2.$$

2nd. *The fluoride is decomposed by* $\mathbf{S}O_2HoKo$, *in the presence of a borate, with formation of volatile boric fluoride*, $\mathbf{B}F_3$.—By heating a mixture* of powdered $\mathbf{S}O_2HoKo$ and fused borax with the finely powdered fluoride, on the loop of a platinum wire, in a clear flame of a Bunsen gas lamp, boric fluoride is disengaged, imparting a beautiful *yellowish green* colour to the flame, which is highly characteristic, although very evanescent.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF SODIC FLUORIDE, NaF.

Most metallic fluorides are solid; others, again, such as the fluorides of the metals whose higher oxides possess acid properties, form volatile, fuming, highly corrosive liquids, or are gaseous at the ordinary temperature.

Fluorides are either soluble in water and more or less crystalline, such as KF, NaF, AmF, AgF, $\mathbf{Sn}F_2$, $\mathbf{Fe}_2F_6$, $\mathbf{Hg}F_2$, or *insoluble in water* and amorphous when obtained by precipitation, *e.g.*, $\mathbf{Ca}F_2$, $\mathbf{Ba}F_2$, $\mathbf{Pb}F_2$, $\mathbf{Zn}F_2$.

---

* 10 eq. of $\mathbf{S}O_2HoKo$ (= 10 × 136).
3 eq. of $\mathbf{Ca}F_2$ (= 3 × 78).
1 eq. of $\mathbf{B}_4O_5Nao_2$ 202.

The reactions which a soluble fluoride gives by *double decomposition* with solutions of salts, whose metals form insoluble fluorides, are not very characteristic.

$\mathbf{Ba}Cl_2$ produces a *bulky white* precipitate of **baric fluoride**, $\mathbf{Ba}F_2$, soluble in hydrochloric acid and in much ammonic chloride.

$\mathbf{Ca}Cl_2$ (or $\mathbf{Ca}Ho_2$) gives a *gelatinous translucent* precipitate of **calcic fluoride**, $\mathbf{Ca}F_2$, which becomes visible by the addition of ammonic hydrate. $\mathbf{Ca}F_2$ is slightly soluble in cold hydrochloric or nitric acid, difficultly soluble in boiling hydrochloric acid, less soluble in acetic acid, insoluble in free hydrofluoric acid, soluble to some extent in ammonic chloride.

$\mathbf{N}O_2Ago$ produces no precipitate. (DISTINCTION BETWEEN HF AND HCl.)

It is preferable to test for HF by the reactions based upon the formation of gaseous $\mathbf{Si}F_4$ or $\mathbf{B}F_3$.

All fluorides (soluble or insoluble) are decomposed on heating with concentrated sulphuric acid, with disengagement of HF, a metallic sulphate being left, thus:—

$$\mathbf{Ca}F_2 + \mathbf{S}O_2Ho_2 = 2HF + \mathbf{S}O_2Cao''.$$

The experiment is best performed by treating the fluoride with sulphuric acid in a small leaden cup (Fig. 86), connected with a leaden still and U-tube, surrounded with ice, for the condensation of the acid.

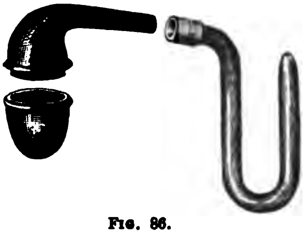


FIG. 86.

Hydrofluoric acid gas is highly corrosive, and should not be inhaled. If it comes in contact with silica (*e.g.*, in glass), $\mathbf{Si}F_4$ is formed. The glass becomes *corroded or etched.*

Its action upon glass may be shown also by covering a platinum crucible, containing a little finely powdered fluoride and concentrated sulphuric acid, with a piece of glass, *e.g.*, a watch-glass. The vapour of the evolved hydrofluoric acid corrodes the glass. The action of the hydrofluoric acid becomes apparent, when the glass is covered with a thin layer of melted wax, and some design scratched on the waxed side with a pointed instrument. The gas acts upon the unprotected portion of the glass. To prevent the melting of the wax, a little cold water is kept on the watch-glass. The design will be found etched more or less deeply into the glass, after the removal of the wax. Mere traces of a fluoride are thus detected, and as no other substance attacks glass similarly, the reaction is perfectly characteristic for hydrofluoric acid.

If the fluoride contain much silica, sulphuric acid disengages silicic fluoride instead of hydrofluoric acid, which does not attack glass; but when passed into water—best by letting the delivery tube dip into a little mercury—it is decomposed into hydrofluosilicic acid and into $\mathbf{Si}Ho_4$, thus:—

$$3\mathbf{Si}F_4 + 4\mathbf{O}H_2 = \mathbf{Si}Ho_4 + 2(2HF, \mathbf{Si}F_4).$$

This reaction is employed for detecting fluorine in silicates, or if applied to fluorides which are free from silica, some finely powdered quartz or glass is first mixed with the fluoride, before treating with sulphuric acid, and passing the silicic fluoride into water.

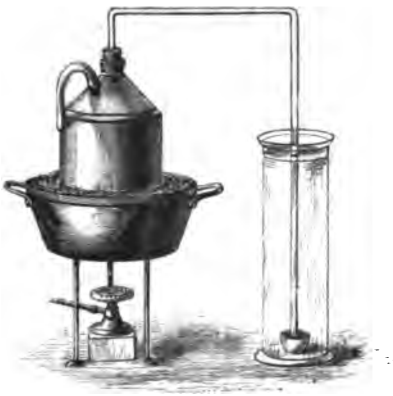


FIG. 87.

The experiment may be performed in a glass flask or small stone ware bottle (Fig. 87), provided with a wide delivery-tube, which dips under mercury contained in a small porcelain cup at the bottom of a beaker or glass cylinder. Care should be taken that the inside of the delivery tube remains perfectly dry, when the receiving vessel is filled with water. A mixture of one part by weight of finely powdered fluorspar, and one by weight of fine sand is introduced into the glass or stone ware vessel. Seven to eight parts by weight of oil of vitriol are added, and the whole shaken up together and gently heated upon a sand- (or water-) bath. Each bubble of the evolved $\mathbf{Si}F_4$, on passing through the water, is decomposed, with separation of gelatinous silica, which after a time fills the whole glass vessel in the form of a dense jelly. The silica is separated by straining through a cloth from the hydrofluosilicic acid, which may be returned to the glass cylinder, and a fresh quantity of $\mathbf{Si}F_4$ passed through, till the acid solution has become sufficiently concentrated.

Silicates which are not decomposed by sulphuric acid, are fused with four parts of fusion mixture. The fused mass is extracted with water and filtered. The filtrate contains the fluorine in the form of alkaline fluorides together with alkaline silicates. On slightly acidulating with dilute hydrochloric acid to decompose the excess of alkaline carbonates, and then digesting with ammonic hydrate, $\mathbf{Si}Ho_4$ is precipitated, which can be filtered off, leaving the alkaline fluoride. On adding $\mathbf{Ca}Ho_2$ or $\mathbf{Ca}Cl_2$, and digesting at a gentle heat, a gelatinous precipitate of $\mathbf{Ca}F_2$ is obtained, which is filtered off, dried, and examined. If phosphoric acid be present, the precipitate contains $\mathbf{P}_2O_2\,Cao''_3$, as well as $\mathbf{Ca}F_2$, which does not, however, interfere with the disengagement of hydrofluoric acid gas.

Insoluble fluorides, *e.g.*, $\mathbf{Ca}F_2$, are not completely decomposed by fusion with alkaline carbonates, unless $\mathbf{Si}O_2$ be present.

QUESTIONS AND EXERCISES.

1. Which are the most important natural compounds of fluorine?
2. What changes do solid fluorides undergo when heated by themselves; 2ndly, when mixed with microcosmic salt or hydric potassic sulphate?
3. How is $\mathbf{B}F_3$ formed, and why does it furnish us with a characteristic reaction for fluorine or *vice versâ* for boron?
4. Classify fluorides according to their solubility in water.
5. Describe some characteristic reactions for fluorine in the wet way.
6. How would you distinguish gaseous HCl from HF?
7. How is hydrofluoric acid gas prepared? Explain its action upon glass.
8. How would you test for small quantities of a fluoride?

9. Explain the action of concentrated sulphuric acid upon a fluoride containing much SiO_2.
10. How is fluorine detected in silicates decomposable by SO_2Ho_2, containing traces of a fluoride?
11. How can fluorine be detected in a mineral containing a silicate which is not decomposed by sulphuric acid, some phosphate, and traces of a fluoride?
12. How would you prepare KF, AmF, 2HF, SiF_4, gaseous, SiF_4, and liquid HF?

HYDROFLUOSILICIC ACID, $2HF,SiF_4$.—Obtained by passing SiF_4 into water and separating the precipitated silica by filtration.

It forms salts called silicofluorides, or fluosilicates, on acting upon metallic oxides, hydrates, or metals, such as Fe or Zn (these latter with evolution of hydrogen), of which the potassic and baric silicofluorides are the most interesting.

REACTIONS IN THE DRY WAY.

Silicofluorides are decomposed by heat into fluorides, with disengagement of SiF_4.

REACTIONS IN THE WET WAY.

A CONCENTRATED SOLUTION OF THE ACID may be employed.

On evaporating a solution of $2HF,SiF_4$ in a platinum vessel, it volatilizes, and is decomposed into SiF_4 and 2HF. The acid ought not, therefore, to be heated in a glass vessel.

A few silicofluorides, e.g., $2KF,SiF_4$, 2NaF, SiF_4, BaF_2, SiF_4, *are difficultly soluble in water, and are rendered quite insoluble by the addition of alcohol.* Most other metallic silicofluorides are readily soluble in water.

$BaCl_2$ precipitates *translucent* crystalline **baric silicofluoride**, BaF_2,SiF_4, which falls out very readily. The precipitation is complete on the addition of an equal volume of alcohol. Strontium is not precipitated from concentrated solutions. (DISTINCTION BETWEEN BARIUM AND STRONTIUM.)

KCl gives a *translucent gelatinous* precipitate of **dipotassic silicofluoride**, $2KF,SiF_4$.

AmHo separates $SiHo_4$ and forms AmF.

On heating a metallic silicofluoride with concentrated sulphuric acid in a platinum crucible, covered with a watch-glass, the glass becomes corroded or etched.

QUESTIONS AND EXERCISES.

1. How is $2HF,SiF_4$ prepared?
2. State how $2HF,SiF_4$ acts upon KHo, OH_2, Fe, CuO.
3. What decomposition takes place when silicofluorides are heated—1st, by themselves; 2ndly, with concentrated SO_2Ho_2?
4. How is BaF_2, SiF_4 obtained?

5. How can strontium and calcium be separated from barium by means of $2HF,\mathbf{Si}F_4$?
6. What proportions by weight of $\mathbf{Ca}F_2$, $\mathbf{Si}O_2$, and $\mathbf{S}O_2Ho_2$, are required for the preparation of $2HF,\mathbf{Si}F_4$?

PHOSPHORIC ACID, $\mathbf{P}OHo_3$.—This acid is never met with in the free state in nature, but invariably in combination with bases, such as $\mathbf{Ca}O$, $\mathbf{Mg}O$, $\mathbf{Al}_2O_3$, $\mathbf{Fe}O$, $\mathbf{Fe}_2O_3$, $\mathbf{Pb}O$, as *bone-ash*, *sombrerite*, *coprolites*, *apatite*, *wagnerite*, *wavellite*, *vivianite*, *pyromorphite*, etc.

Its most characteristic properties have already been described (Chap. XVI).

REACTIONS IN THE DRY WAY.

Normal phosphates of fixed bases are not decomposed upon ignition. Mono- and di-hydric normal phosphates lose water, and are converted into pyro- and metaphosphates, thus:—

$$(1)\quad 2\mathbf{P}OHoNao_2 = \underset{\substack{\text{Sodic}\\ \text{pyrophosphate.}}}{\mathbf{P}_2O_3Nao_4} + \mathbf{O}H_2.$$

$$(2)\quad \mathbf{P}OHo_2Nao = \underset{\substack{\text{Sodic}\\ \text{metaphosphate.}}}{\mathbf{P}O_2Nao} + \mathbf{O}H_2.$$

Fusion with caustic or carbonated alkalies converts pyro- and metaphosphates into normal or orthophosphates. Boiling with concentrated acids ($\mathbf{N}O_2Ho$) effects this conversion likewise.

Alkaline earthy phosphates are only partially decomposed by fusion with alkaline carbonates; most others, *e.g.*, magnesic, ferric, zincic, nickelous, manganous, cupric, phosphates are completely decomposed. The solution contains trisodic and tripotassic phosphates. $\mathbf{P}_2O_2Al_2o^{vi}$ can only be decomposed by fusion with silicic anhydride or sodic silicate (water-glass) and fusion mixture,* being converted into sodic aluminic silicate and trisodic phosphate.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF HYDRIC DISODIC PHOSPHATE, $\mathbf{P}OHoNao_2$.

All phosphates may be divided into—

1st. *Phosphates which are soluble in water*, comprising the alkaline phosphates only; and

2nd. *Phosphates which are insoluble in water, but soluble in mineral acids* (some also in acetic acid), comprising all other metallic phosphates.

The following are some of the more important reactions by double decomposition:—

$\mathbf{Ba}Cl_2$ yields a *white* precipitate of **hydric baric phosphate**, $\mathbf{P}OHoBao''$, difficultly soluble in ammonic chloride, soluble in nitric or hydrochloric acid.

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* One part of $\mathbf{Si}O_2$, together with six parts of fusion mixture.

$CaCl_2$, or SO_2Cao'' produces a *white* precipitate of **hydric calcic phosphate**, $POHoCao''$, readily soluble in mineral acids,[*] soluble in acetic acid, after being freshly precipitated, difficultly soluble in ammonic chloride.

SO_2Mgo'' (or $MgCl_2$) in the presence of AmCl and AmHo produces a *white crystalline* precipitate of **ammonic magnesic phosphate**, $POAmoMgo'' + 6$ aq., insoluble in ammonic hydrate, readily soluble in acids, even acetic acid. A dilute solution of sodic phosphate is only precipitated after some time. The precipitation is promoted by stirring and allowing the liquid to stand in a warm place, when the precipitate is seen to adhere in the form of white streaks, more especially to those parts of the glass vessel which have been touched by the glass rod.

This is the most important reaction for $POHo_3$, which is almost invariably resorted to, both for the recognition of MgO and $POHo_3$.

NO_2Ago gives a *yellow* precipitate of **triargentic phosphate**, $POAgo_3$, soluble in ammonic hydrate and in nitric acid.

$\left(\begin{cases}CH_3\\CO\end{cases}\right)_2Pbo''$, **plumbic acetate**, produces a *white* precipitate of **plumbic phosphate**, $P_2O_2Pbo''_3$, readily soluble in nitric acid, almost insoluble in acetic acid, as well as ammonic hydrate. If the precipitate is fused before the blowpipe on charcoal, the bead appears *crystalline* on cooling; *no reduction to the metallic state* takes place.

Fe_2Cl_6 gives a *yellowish white gelatinous* precipitate of **ferric phosphate**, $P_2O_2Fe_2o^{vi}$, soluble in hydrochloric acid. The ferric salt should be added drop by drop, sufficient to just impart a red tinge to the supernatant solution, since the precipitate is soluble in excess of ferric chloride. Sodic acetate must be added to remove the two molecules of free hydrochloric acid which would otherwise dissolve some of the precipitate.

When phosphoric acid has to be removed from a phosphate dissolved in hydrochloric acid, *e.g.*, from the alkaline earthy phosphate, $P_2O_2Cao''_3$, the free acid is nearly neutralized with ammonic hydrate or ammonic carbonate, and then sodic acetate added, which, by double decomposition with the free hydrochloric acid, forms sodic chloride and free acetic acid, in which the precipitate, produced by *a slight excess* of ferric chloride, is absolutely insoluble. The mixture is heated to boiling, a reddish brown precipitate is obtained, which contains the whole of the phosphoric acid. It must be filtered hot, and washed with hot water, the filtrate contains the alkaline earthy bases as chlorides.

$AsOHo_3$ exhibits with ferric chloride a similar reaction, and has, therefore, to be separated from a HCl solution, by boiling with $SOAmo_2$ and precipitation by a current of SH_2 gas.

Small *traces of phosphorus* (phosphoric acid), usually found in iron ores, in pig iron, steel, sheet copper, etc., are best precipitated after dissolving the ore or metal in hydrochloric and nitric acids, whereby the phosphorus is converted into $\mathbf{P}OHo_3$, by adding a solution of ammonic molybdate and free nitric acid; the silicic acid should be separated by evaporation to dryness, and arsenic acid, if present by sulphuretted hydrogen. On digesting the solution at a gentle heat (60° C.) for some time (hours if necessary), and stirring with a glass rod, a *bright yellow* precipitate of **ammonic phosphomolybdate** is obtained.

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[*] $P_2O_2Cao''_3 + 4NO_2Ho = P_2O_2Ho_4Cao'' + 2\begin{matrix}NO_2\\NO_2\end{matrix}Cao''$.

Soluble tetrahydric
calcic diphosphate, reprecipitated by AmHo.

The constitution of this precipitate is not well understood; we know merely that it contains molybdic acid, ammonia and phosphoric acid* (about 3 per cent). On dissolving the yellow precipitate in ammonic hydrate, filtering, and adding $\mathbf{S}O_2Mgo''$, AmCl, and AmHo, the phosphoric acid is obtained as $\mathbf{P}OAmoMgo''$.

White of egg (albumen) is not coagulated by tribasic phosphoric acid, nor by a solution of an orthophosphate acidulated with acetic acid.

PYROPHOSPHORIC ACID, $\mathbf{P}_2O_3Ho_4$.—Pyrophosphates are obtained by heating monohydric phosphates. They are of little importance, however, since they are not usually met with in natural compounds, and as they are speedily converted, by the action of acids or alkalies, into tribasic phosphates.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF SODIC PYROPHOSPHATE, $\mathbf{P}_2O_3Nao_4$.

Alkaline pyrophosphates are soluble in water.

All others are insoluble in water, but soluble in dilute acids.

The presence of a soluble pyrophosphate is indicated on adding $\mathbf{N}O_2Ago$, which gives a *white* precipitate of **argentic pyrophosphate,** $\mathbf{P}_2O_3Ago_4$, soluble in nitric acid and ammonic hydrate.

Albumen is not coagulated by the free acid, nor by an acetic solution of a pyrophosphate.

$\mathbf{M}o_2Amo_2$ does not give a precipitate, until by the action of mineral acids the pyrophosphate has been converted into tribasic phosphate.

METAPHOSPHORIC ACID, $\mathbf{P}O_2Ho$, is distinguished from the tetra- and tribasic acid as follows:—

Albumen gives an abundant *white* precipitate with the free acid, and with soluble metaphosphates, on the addition of acetic acid.

$\mathbf{S}O_2Mgo''$, AmCl and AmHo fail to precipitate soluble metaphosphates.

In the ordinary course of analysis both pyro- and metaphosphates are converted into tribasic phosphates, and their tetrabasic and monobasic nature is lost sight of. They can, therefore, only be detected by special experiments.

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* $\mathbf{M}o_2O_3$, 90·7 P.C; $\mathbf{P}_2O_5$, 3·1 P.C; $\mathbf{O}Am_2$, 3·6 P.C, and $\mathbf{O}H_2$, 2·6 P.C.

PHOSPHOROUS ACID, $\mathbf{P}OHHo_2$, (dibasic).—The formation of phosphorous anhydride by the action of dry air upon phosphorus has already been mentioned. By combining with water it forms a very weak acid, and with hydrated alkalies alkaline phosphites.

REACTIONS IN THE DRY WAY.

Heated by themselves on platinum foil, *phosphites* are decomposed, burning with a bright flame. Heated in a retort they evolve hydrogen, mixed towards the end of the decomposition with $\mathbf{P}H_3$, and are converted into phosphates.

REACTIONS IN THE WET WAY.

A SOLUTION OF SODIC PHOSPHITE, $\mathbf{P}OHNao_2$, may be employed.

Alkaline phosphites are soluble in water.

All other phosphites are, for the most part, difficultly soluble or insoluble in water, but soluble in acetic acid ($\mathbf{P}OHPbo''$ excepted). Phosphites (as well as hypophosphites) are of interest mainly on account of the powerful reducing action which they exert upon salts of various metallic oxides, capable of forming lower oxides, or of being reduced to the metallic state, as well as upon the lower oxides, etc., of metalloids, *e.g.*, $\mathbf{S}O_2$.

$\mathbf{N}O_2Ago$ is reduced thereby to metallic silver, especially in the presence of ammonia and on the application of a gentle heat.

$\mathbf{Hg}Cl_2$ and $\mathbf{N}_2O_4Hg_2o''$ are reduced to $\mathbf{Hg}_2Cl_2$ and metallic mercury.

$\mathbf{S}O_2$ forms a phosphate with liberation of sulphur and evolution of $\mathbf{S}H_2$.

Nascent hydrogen yields a mixture of H and $\mathbf{P}H_3$ which fumes in the air and burns with an emerald green colour. When passed into a solution of argentic nitrate, the gaseous mixture precipitates $\mathbf{P}Ag_3$ and metallic silver.

The insoluble phosphites of Ba, Ca, Pb, etc., are obtained by double decomposition, the latter salt being insoluble in acetic acid.

HYPOPHOSPHOROUS ACID, $\mathbf{P}OH_2Ho$ (monobasic).—Obtained by the action of alkalies or hydrates of the alkaline earthy bases upon phosphorus and water.

$$P_4 + 3\mathbf{O}H_2 + 3KHo = 3\mathbf{P}OH_2Ko + \mathbf{P}H_3.$$

REACTIONS IN THE DRY WAY.

Hypophosphites are decomposed upon ignition into pyrophosphates and $\mathbf{P}H_3$.

$$4\mathbf{P}OH_2Ko = \mathbf{P}_2O_3Ko_4 + 2\mathbf{P}H_3 + \mathbf{O}H_2.$$

REACTIONS IN THE WET WAY.

A SOLUTION OF POTASSIC HYPOPHOSPHITE may be employed.

All hypophosphites are soluble in water. They constitute even more powerful reducing agents than the phosphites.

Nitric acid or chlorine water changes them into phosphates.

$\mathbf{S}O_2Ho_2$ is reduced to $\mathbf{S}OHo_2$, partly even to sulphur.

$\mathbf{S}O_2Cuo''$ is reduced to metallic copper.

$\mathbf{Hg}Cl_2$ is reduced to $\mathbf{Hg}_2Cl_2$, and then to mercury.

$\mathbf{Au}Cl_3$ and $\mathbf{N}O_2Ago$ yield the pure metals.

Zn + $\mathbf{S}O_2Ho_2$ (nascent hydrogen) yield H and $\mathbf{P}H_3$.

In the ordinary course of analysis, both phosphorous and hypophosphorous acids are converted into phosphoric acid, and they must therefore be identified by the special reactions just described.

QUESTIONS AND EXERCISES.

1. How does phosphoric acid occur in nature?
2. Explain the action of heat upon $\mathbf{P}OHo_2Nao$, $\mathbf{P}OAmoMgo''$, and $\mathbf{P}OHoAmoNao$.
3. How are meta- and pyrophosphates converted into tribasic phosphates?
4. Explain the action of potassic hydrate or carbonate upon $\mathbf{P}_2O_2Fe_2o^{vi}$, $\mathbf{P}_2O_2Cao''_3$, $\mathbf{P}_2O_2Cuo''_3$, $\mathbf{P}OHoBao''$, in the wet and dry way.
5. How can $\mathbf{P}_2O_2Al_2o^{vi}$ be decomposed?
6. Classify all phosphates, pyrophosphates, phosphites, and hypophosphites according to their solubility in water.
7. Explain the solvent action of HCl or $\mathbf{N}O_2Ho$ upon the alkaline earthy phosphates.
8. How is phosphoric acid removed from alkaline earthy phosphates?
9. State how you would detect traces of phosphoric acid in a soil, or phosphorus in metallic copper or cast iron.
10. What is the approximate composition of ammonic phospho-molybdate?
11. Which reactions enable us to distinguish between tribasic, tetrabasic and monobasic phosphates?
12. How would you prove the presence of magnesic, as well as of potassic phosphates in wheat flour, in pale ale, and in cheese?
13. How would you prepare $\mathbf{P}OH_2Ho$ and $(\mathbf{P}OH_2)_2Cao''$?
14. How are calcic phosphite and potassic hypophosphite acted upon by heat?
15. What are the products of oxidation obtained on burning $\mathbf{P}H_3$ in air?
16. Explain the deoxidizing action of phosphites and hypophosphites.
17. How can potassic hypophosphite be detected in the presence of potassic phosphite and phosphate?
18. How would you prepare gaseous $\mathbf{P}H_3$? What is its action upon solutions of cupric sulphate and argentic nitrate?
19. Give symbolic and graphic formulæ for gaseous phosphoretted hydrogen, calcic hypophosphite, cupric phosphide.
20. Express by a symbolic equation the change which $\mathbf{P}OHHo_2$ undergoes when it is acted upon by $\mathbf{S}O_2Ho_2$, by $\mathbf{S}O_2Cuo''$, or by $\mathbf{Au}Cl_3$.
21. How would you convert bone-ash into a soluble calcic phosphate (into $\mathbf{P}_2O_2Ho_4Cao''$—a constituent of calcic superphosphate)?
22. 5·4 grms. of cast iron yielded ·046 of $\mathbf{P}_2O_3Mgo''_2$; what is the percentage of phosphorus in the iron?

SILICIC ACID, $\mathbf{Si}Ho_4$.—*Silicic anhydride or silica*, $\mathbf{Si}O_2$, occurs in nature both in a *crystalline* and *amorphous* condition, either in the free or combined state. *Quartz* and *rock crystal* are composed of almost pure crystalline silica. *Opal*, *hyalite*, and some other minerals consist of amorphous silica, and are probably derived from silicic hydrate by a process of slow dehydration. Other silicious bodies, such as *chalcedony*, *agate*, *flint*, are principally composed of amorphous silica, or of a mixture of the two.

The compounds of silica with bases, especially with $\mathbf{O}K_2$, $\mathbf{O}Na_2$, $\mathbf{Ca}O$, $\mathbf{Mg}O$, $\mathbf{Al}_2O_3$, $\mathbf{Fe}O$, $\mathbf{Mn}O$, are exceedingly numerous, and vary to a very great extent in their constitution and properties.

REACTIONS IN THE DRY WAY.

Both varieties of silica are characterized by their infusibility when heated by themselves before the blowpipe, or in a bead of microcosmic salt. Pure silica fuses with sodic carbonate to a clear glass, which remains transparent on cooling. If a silicate be heated in like manner, its base or bases are dissolved by the microcosmic salt, while the silica is seen to float about in the liquid bead as a *silica skeleton*. Silicates containing coloured oxides give rise to opalescent beads, in which the $\mathbf{Si}O_2$ can be distinguished only with difficulty.

When silica, or a silicate rich in silica, is heated before the blowpipe with sodic carbonate, the $\mathbf{Si}O_2$ displaces the $\mathbf{C}O_2$, and forms a clear glass of sodic silicate. The alkaline carbonate should not be employed in excess. Calcic and magnesic silicates do not dissolve to a clear bead as a rule.

Beyond identifying silica and obtaining a general knowledge of the nature of any silicate under examination, respecting its fusibility, state of hydration, etc., the blowpipe reactions fail to supply distinguishing tests regarding the chemical composition of these bodies, since a very large number of silicates differ from each other merely in the relative proportions of their component metallic elements.

REACTIONS IN THE WET WAY.

All silicates may be divided into—

1. *Silicates* which are *soluble in water*, including only potassic and sodic silicate; and
2. *Silicates*, *insoluble in water*, including all others.

These latter silicates are either *soluble* in concentrated hydrochloric or sulphuric acid, or *partly soluble* and *partly insoluble*, or lastly, *insoluble in these acids*.

All insoluble silicates are attacked by hydrofluoric acid, with disengagement of silicic fluoride, or by fusion mixture (or caustic baryta) at a high temperature.

By treating an aqueous solution of sodic silicate, $\mathbf{Si}Nao_4$, with dilute hydrochloric acid, it is decomposed into NaCl and $\mathbf{Si}Ho_4$. The latter remains either dissolved in the acid, or is partially separated as a flaky or gelatinous mass. On evaporating in a porcelain dish over a water-bath, the gelatinous mass becomes firmer, and can be broken up, by means of a glass rod, into lumps, which speedily lose their water, leaving *anhydrous* silica, especially on being ignited on a sand-bath, as long as acid fumes are evolved. The dried mass is treated with a little concentrated hydrochloric acid and hot water, when NaCl is dissolved out (together with small quantities of Al and Fe—impurities in the sodic silicate). The impalpable powder of amorphous silica is thrown on a filter and washed with hot water, dried and ignited (comp. Exp. 92).

AmCl and $\mathbf{C}OAmo_2$ precipitate $\mathbf{Si}Ho_4$ from a solution of sodic silicate. Salts of most of the heavy metals, as well as of the alkaline earthy metals, form by double decomposition with a soluble silicate, white or yellowish white silicates, soluble in dilute hydrochloric or nitric acid, which, however, possess no characteristic properties. It is, therefore, necessary to remove the silica in order to detect bases, by evaporating to dryness with hydrochloric acid. On digesting the dry mass with a little hydrochloric acid, the metallic oxides are dissolved, and can be separated by filtration from the silicic anhydride. $\mathbf{Si}O_2$, *like* $\mathbf{P}_2O_5$, *is detected whilst testing for bases.*

Most silicates are insoluble in water. Many of the natural silicates, *e.g.*, zeolites, as well as certain artificial silicates, such as slags from blast furnaces, etc., are decomposed on digesting the finely powdered silicate with concentrated hydrochloric acid. The gelatinous mass is evaporated to dryness on a water-bath, when amorphous silica separates.

Silicates, such as kaolin, *which are not dissolved by hydrochloric acid, can frequently be decomposed, either partly or wholly, by hot concentrated sulphuric acid;* many natural silicates yield more or less silica, on treatment with hydrochloric acid, which silica may be taken to represent the soluble silica or the decomposable silicates, leaving the greater portion of the mineral behind in an insoluble condition.

Silica, or silicates insoluble in acids, *are readily attacked by gaseous hydrofluoric acid* or $\mathbf{Ca}F_2$ (Fluorspar) and $\mathbf{S}O_2Ho_2$, *gaseous* $\mathbf{Si}F_4$ *being given off.* This method is invariably resorted to whenever alkalies are present in a silicate, as *e.g.*, in felspar, $\mathbf{Si}_6O_8Ko_2Al_2o^{vi}$. A little of the finely powdered silicate is moistened with strong ammonia, put into a platinum crucible or small platinum capsule, and exposed to the action of gaseous HF. This gas should be generated in a leaden or platinum vessel. The platinum crucible is to this end placed in a small leaden vessel, which can be closed with a lid of the same metal. A layer of fluorspar is put at the bottom of this vessel, mixed and covered with concentrated sulphuric acid. The platinum crucible rests on a leaden tripod. The leaden vessel after being covered and luted with moist linseed meal, is placed for a day or two in a warm place. The crucible is then taken out, and its contents cautiously evaporated by applying a gentle heat, as shown in Fig. 88, from the upper part of the crucible downward, till the whole of the ammonic fluoride has been driven off. The dry residue is dissolved in hydrochloric acid, and tested for bases. A small residue is usually left, which is filtered off and treated once more in the same manner.

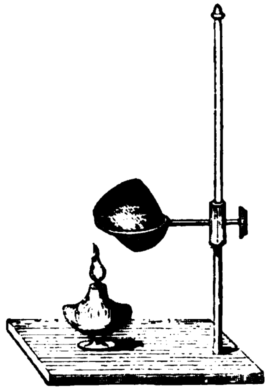

FIG. 88.

The same result may be obtained more expeditiously by treating the mineral in a platinum crucible with *liquid hydrofluoric acid,* and evaporating cautiously in a closet which stands in connection with the chimney, and which has a good in-draught of air. The residue is dissolved in hydrochloric acid. Any insoluble residue which may be left is separated by filtration and treated again with hydrofluoric acid. This treatment has generally to be repeated several times, before the whole of the bases are obtained in a soluble condition.

Treatment with $\mathbf{Ca}F_2$ and concentrated $\mathbf{S}O_2Ho_2$ is objectionable, on account of the formation of insoluble $\mathbf{S}OHo_2Cao''$.

All silicates insoluble in water and acids, no matter whether they contain alkali metals or not, *may be decomposed by fusion with alkaline carbonates* (fusion mixture). They are first ground up very finely in an agate mortar, then intimately mixed with three to four times their weight of fusion mixture and heated in a platinum crucible as long as any $\mathbf{C}O_2$ is given off. This may be done over a good Bunsen gas lamp or by means of a Herapath gas blowpipe. (A platinum crucible can be employed with safety only when the absence of easily reducible and fusible metals has been established by a preliminary examination of the silicious substance in the dry way.) The silica is thus obtained in combination with the alkalies and dissolves in hot water, and the bases ($\mathbf{Ca}O$, $\mathbf{Mg}O$, $\mathbf{Al}_2O_3$, $\mathbf{Fe}_2O_3$, etc., etc.) are left as insoluble oxides or carbonates, and may be separated by filtration; or the whole mass is at once treated with dilute hydrochloric acid and evaporated to dryness. Silicic anhydride is left, and the bases are removed as chlorides by filtration. It is obvious that we must examine for the alkali bases in a separate portion, by treatment with hydrofluoric acid.

Pure amorphous silica dissolves completely, when boiled in a platinum vessel with an aqueous solution of fixed caustic or carbonated alkalies.

$\mathbf{Si}O_2$ is separated from $\mathbf{Ti}O_2$ (titanic anhydride) by fusion with $\mathbf{S}O_2HoKo$ in a platinum crucible, and subsequent treatment with water; the $\mathbf{Si}O_2$ remains undissolved. The $\mathbf{Ti}O_2$ is precipitated from the acidulated aqueous solution by long-continued boiling.

QUESTIONS AND EXERCISES.

1. Give instances of crystalline and amorphous silica.
2. Describe the reactions for $\mathbf{Si}O_2$ in the dry way.
3. Classify silicates according to their solubility in water and acids.
4. Explain the action of HF, or of $\mathbf{Ca}F_2$ and concentrated $\mathbf{S}O_2Ho_2$ upon silicates.
5. Describe how amorphous silica is obtained from $\mathbf{Si}Nao_4$, from quartz, or from felspar.
6. How would you ascertain the presence of potassium or sodium in a silicate soluble in HCl, and in a silicate insoluble in HCl, *e.g.*, in Bohemian glass?
7. What is the action of caustic and carbonated alkalies upon amorphous silica?
8. How is $\mathbf{Ti}O_2$ separated from $\mathbf{Si}O_2$?
9. How is silicon detected in pig iron?

BORIC ACID, $\mathbf{B}Ho_3$ (orthoboric acid).—Is found in nature, both combined and in the free state. Its preparation from borax has already been described, as well as its most characteristic properties. (Comp. Chap. XVII., Part I.)

REACTIONS IN THE DRY WAY.

Most borates swell up when heated by themselves, and fuse into a transparent glass which dissolves metallic oxides, producing various colours. The free acid forms scaly crystals, possessing a pearly lustre and feeling peculiarly greasy to the touch. When heated to 100° C. the crystals lose water and become converted into metaboric acid, $BOHo$. This acid fuses to a colourless, transparent, glassy looking mass,—*boric anhydride*, B_2O_3, which can be kept in a liquid condition without loss from volatilization.

A mixture of SO_2HoKo and a borate, heated on a platinum wire in a blowpipe flame, imparts a green colour to the flame, owing to the liberation of boric acid.

To detect *traces* of boric acid before the blowpipe, the borate is powdered and mixed with SO_2HoKo and CaF_2.[*] (Comp. page 260.) The mixture is made into a stiff paste with a few drops of water, and cautiously introduced on the loop of a platinum wire into the *inner* blowpipe flame, when the outer flame acquires momentarily a *yellowish green tint*, owing to the volatilization of boric fluoride, BF_3. Phosphates as well as copper salts, when moistened with sulphuric acid and heated in the *outer* flame, give likewise a green tint to the flame.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF BORAX, $B_4O_6Nao_2$.

The alkaline borates are soluble in water, all others are difficultly soluble, but none are absolutely insoluble. All borates dissolve in acids and ammonic chloride.

The precipitates produced by double decomposition of a soluble alkaline borate with salts of the alkaline earths, or with plumbic, argentic, mercurous, or ferrous salts, etc., are *white* or *yellowish white*, and are readily soluble in acids and ammonic chloride.

The *free* acid dissolves in water and alcohol, and its solutions impart to a Bunsen gas flame a *fine green* colour. An alcoholic solution placed in a porcelain dish burns with the same characteristic flame, and the colour becomes all the more perceptible, when the burning alcohol is stirred with a glass rod. It does not show in the presence of alkaline hydrates or carbonates, or of any other base. The reaction is equally vitiated by the presence of sodic or calcic chloride, or even by the presence of small quantities of an alkaline tartrate, free tartaric or phosphoric acid; but the green colour becomes again perceptible on the *addition of a little concentrated sulphuric acid.*

A green flame (of a somewhat greenish blue tint, however) is obtained also by heating many metallic chlorides with alcohol and concentrated sulphuric acid (owing to the formation of ethylic chloride, $\left\{\begin{matrix}CH_3\\CH_2Cl\end{matrix}\right.$), also by passing hydrochloric acid gas into the flame of burning alcohol.

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[*] Three to four parts of the flux (consisting of one part of powdered CaF_2 and four and a half to five parts of SO_2HoKo).

Boric acid, when combined with bases, requires first to be liberated, by the addition of a little concentrated sulphuric acid, before its alcoholic solution can produce the green flame.

If a borate is not decomposed by sulphuric acid, it is fused with potassic hydrate, and the fused mass taken up with alcohol. On the addition of concentrated sulphuric acid the burning alcohol shows the characteristic green flame.

An aqueous solution of boric acid cannot be evaporated without loss of the acid from volatilization.

An alcoholic solution of boric acid *colours turmeric paper reddish brown*, especially on drying the strips of paper in a warm place (a water-oven). This colour becomes more intense in the presence of hydrochloric or sulphuric acid (even in the presence of nitric or tartaric acid). The colour produced by heating turmeric paper with hydrochloric acid is blackish brown, and must not be confounded with the colour produced by boric acid. The dried paper acquires a blackish tint when dipped into alkalies.

Hydrofluoric acid (or $\mathbf{S}O_2Ho_2$ and $\mathbf{Ca}F_2$), decomposes all borates, with formation of volatile boric fluoride, thus:—

$$\mathbf{B}_4O_5Nao_2 + 6\mathbf{Ca}F_2 + 7\mathbf{S}O_2Ho_2 = 6\mathbf{S}OHo_2Cao'' + \mathbf{S}O_2Nao_2 + 4\mathbf{B}F_3 + \mathbf{O}H_2,$$

and if the gaseous boric fluoride be passed into water, it forms a peculiar acid—*hydrofluoboric acid*—the constitution of which is not well understood, thus:—

$$4\mathbf{B}F_3 + 3\mathbf{O}H_2 = \underset{\substack{\text{Hydrofluoboric}\\ \text{acid.}}}{3(BF_3,HF)} + \mathbf{B}Ho_3.$$

This acid combines with bases, forming *borofluorides* or *fluoborates*, thus:—

$$BF_3,HF + KHo = BF_3,KF + \mathbf{O}H_2.$$

QUESTIONS AND EXERCISES.

1. How is metaboric acid obtained?
2. Explain the reactions in the dry way for boric acid or borates.
3. Classify borates according to their solubility in water.
4. Explain the colour test for boric acid.
5. How are borates, insoluble in water, examined?
6. Explain the action of HF upon boric acid.
7. State how you would prepare argentic borate, plumbic borate, hydrofluoboric acid, and potassic fluoborate.
8. Explain the action of boric acid upon turmeric paper.
9. What is the weight of one litre of $\mathbf{B}F_3$ gas?

HYDROCYANIC ACID, (Prussic acid) HCy.—This acid consists of hydrogen and the compound radical cyanogen, Cy, molecule $\left\{\begin{matrix} {}'\mathbf{C}'''N''' \\ {}'\mathbf{C}'''N''' \end{matrix}\right.$. It forms with metallic oxides salts, called *cyanides*, analogous in their chemical constitution to chlorides, bromides, etc. Cyanogen cannot be obtained by the direct combination of carbon and nitrogen, but an alkaline cyanide results from the action of caustic or carbonated alkalies upon nitrogenous organic bodies, such as fibrin, albumen, and gelatin at a high temperature. The best known cyanide, viz., potassic cyanide, KCy, unless specially purified, contains more or less potassic cyanate, CyKo, and potassic carbonate.

REACTIONS IN THE DRY WAY.

KCy and NaCy are not decomposed upon ignition in close vessels, as may be inferred from their mode of manufacture; but when heated with free access of air, they are converted into cyanates. The same change takes place, only more speedily, when potassic cyanide is heated with an oxidizing agent, such as $\mathbf{Mn}O_2$, $\mathbf{Pb}O$, $\mathbf{Cu}O$, $\mathbf{Sn}O_2$, etc., when the metal, or a lower oxide is left. Heated in the presence of metallic sulphides, it is converted into potassic sulphocyanate, CyKs. Potassic cyanide is on this account a most valuable deoxidizing (desulphurizing) agent, and is employed in blowpipe reactions, whenever a metallic oxide or sulphide has to be reduced to the metallic state. Cyanides of the heavy metals undergo decomposition upon ignition; some (*e.g.*, the cyanides of the noble metals) break up into metal and cyanogen gas; others into a metallic carbide and nitrogen (*e.g.*, the cyanides of iron); others again (such as AgCy, $\mathbf{Hg}Cy_2$, $\mathbf{Cu}Cy_2$, $\mathbf{Zn}Cy_2$) yield cyanogen gas, metallic silver, mercury, etc., and paracyanogen,—a brownish black substance, which is isomeric with cyanogen, and which is usually expressed by the symbol, Cy_n.

This deportment of solid cyanides furnishes us with ready means of preparing cyanogen gas, either by *igniting dry* $\mathbf{Hg}Cy_2$ or AgCy; or *by heating two parts of dry yellow prussiate of potash,* or commercial potassic ferrocyanide, K_4FeCy_6, *with three parts by weight of dry* $\mathbf{Hg}Cl_2$.

Cyanogen is a colourless gas, of peculiar odour, burning with a beautiful purple or peach-blossom coloured flame, and yielding $\mathbf{C}O_2$ and N. The gas is nearly twice as heavy as air (sp. gr. 1·8), and since water dissolves about four times its own volume it must be collected over mercury, or by downward displacement. It is one of the few gases which condense at a moderate pressure (3·6 atmospheres).

REACTIONS IN THE WET WAY.

The *cyanides of the alkali metals and alkaline earthy metals are soluble in water,* the former readily, the latter with difficulty. The *cyanides of the heavy metals are insoluble in water,* with the exception of $\mathbf{Hg}Cy_2$; but are for the most part soluble in a solution of potassic cyanide, forming soluble *double cyanides,* which are frequently crystalline, and which upon ignition are decomposed like single cyanides, *i.e.*, the cyanide of the heavy metal breaks up into metal and cyanogen, or metal, carbon (carbide?) and nitrogen, whilst the alkaline cyanide is not decomposed, and can be dissolved out from the residue.

The following is a list of some of the more important single cyanides, *i.e.*, cyanides which contain only one metal:—

Potassic	cyanide,	soluble in water	KCy
Sodic	„	„ „	$NaCy$
Baric	„	difficultly soluble in water	$\mathbf{Ba}Cy_2$
Zincic	„	insoluble in water	$\mathbf{Zn}Cy_2$
Cadmic	„	„ „	$\mathbf{Cd}Cy_2$
Nickelous	„	„ „	$\mathbf{Ni}Cy_2$
Cobaltous	„	„ „	$\mathbf{Co}Cy_2$
Ferrous	„	„ „	$\mathbf{Fe}Cy_2$
Cuprous	„	„ „	$'\mathbf{Cu}'_2Cy_2$
Mercuric	„	soluble in water	$\mathbf{Hg}Cy_2$
Argentic	„	insoluble in water	$\mathbf{Ag}Cy$.

Some of these single cyanides are readily decomposed by acids, with evolution of hydrocyanic acid; others, especially the cyanides of iron, cobalt, and the noble metals (Au,Pt), may be boiled with moderately strong acids, without decomposition.

The action of dilute acids upon double cyanides shows clearly the existence of two distinct classes of double cyanides, viz.:—

1st. *Double cyanides which are readily decomposable, giving off hydrocyanic acid, when heated with dilute mineral acids.* They possess an alkaline reaction. Their alkaline cyanide is decomposed by dilute mineral acids into HCy and a salt of the alkali metal, and into a cyanide of the heavy metal, which remains in combination with the liberated HCy; or the latter is evolved and the metallic cyanide is precipitated; or both cyanides are decomposed, and the whole of the HCy is liberated, *e.g.*:—

$$(1)\ KAgCy_2 + \mathbf{N}O_2Ho = \underset{\text{Precipitated.}}{AgCy} + HCy + \mathbf{N}O_2Ko.$$

$$(2)\ K_2Zn''Cy_4 + 4HCl = \mathbf{Zn}Cl_2 + 2KCl + 4HCy.$$

2nd. *Double cyanides which possess a neutral reaction and give off no hydrocyanic acid, when treated with dilute hydrochloric acid; the negative element of the acid forming a salt with the alkali metal,* whilst the hydrogen or positive element, by uniting with the remaining elements, forms a new acid of a more complex nature, thus:—

$$K_4FeCy_6 + 4HCl = \underset{\substack{\text{Hydroferrocyanic}\\ \text{acid.}}}{H_4FeCy_6} + 4KCl.$$

$$K_6Fe_2Cy_{12} + 6HCl = \underset{\substack{\text{Hydroferricyanic}\\ \text{acid.}}}{H_6Fe_2Cy_{12}} + 6KCl.$$

$$K_6Co_2Cy_{12} + 6HCl = \underset{\substack{\text{Hydrocobalticyanic}\\ \text{acid.}}}{H_6Co_2Cy_{12}} + 6KCl.$$

The single, as well as easily decomposable double cyanides, which yield hydrocyanic acid, when treated with dilute mineral acids, are moreover remarkable for their highly poisonous character, whilst these latter—the double cyanides containing a non-decomposable cyanogen radical (*e.g.*, *ferrocyanogen*, $FeCy_6$, *cobalticyanogen*, Co_2Cy_{12})—are not poisonous.

It is obvious that all these complex cyanogen compounds—both decomposable and non-decomposable—may likewise be viewed as double cyanides.

The following list* contains some of the more interesting double cyanides, *i.e.*, cyanides containing more than one metal; the *easily decomposable* class being indicated by a comma placed between the cyanogen and the metal:—

Dipotassic zincic tetracyanide	K_2Zn,Cy_4.
„ cadmic „	K_2Cd,Cy_4.
„ nickelous „	K_2Ni,Cy_4.
Potassic argentic dicyanide	KAg,Cy_2.
„ aurous „	KAu',Cy_2.
„ auric tetracyanide	KAu''',Cy_4.
Dipotassic cuprous tetracyanide	$K_2'Cu'_2,Cy_4$.
„ platinous „	K_2Pt'',Cy_4.
Tetrapotassic diplatinic decacyanide	$K_4,'Pt'''_2Cy_{10}$.
„ ferrous hexacyanide (potassic ferrocyanide, *yellow prussiate*)	$K_4,FeCy_6$.
Hexapotassic diferric dodecacyanide (potassic ferricyanide, *red prussiate*)	K_6,Fe_2Cy_{12}.
Hexapotassic dicobaltic dodecacyanide (potassic cobalticyanide)	K_6,Co_2Cy_{12}.
Hexapotassic dichromic dodecacyanide	K_6,Cr_2Cy_{12}.
„ dimanganic „	K_6Mn_2,Cy_{12}.

If we take, however, into account the different deportment of these double cyanides with dilute acids and with ferroso-ferric salts, with which the easily decomposable double cyanides give, from an acid solution, a precipitate of Prussian blue, whilst the others—the difficultly decomposable double cyanides—yield no hydrocyanic acid when treated with dilute acids, and produce (with the exception of the ferro- and ferricyanogen compounds), no precipitate of Prussian blue with ferroso-ferric salts and hydrochloric acid, it becomes evident *that the complex groups of elements*, *ferrocyanogen*, $FeCy_6$, *ferricyanogen*, Fe_2Cy_{12}, *cobalticyanogen*, Co_2Cy_{12}, etc., *which behave like cyanogen* (itself a complex group of two elements, of carbon and nitrogen, or a compound radical) *may likewise be viewed as compound radicals*, if by this term we denote a group of common and constant constituents found in a whole series of compounds, and capable of replacing multiples of Cl, Br, etc., in constant atomic proportions.

We are able, for instance, to produce by double decomposition, precipitates with soluble salts of almost all the heavy metals in which the potassium—or positive radical—is either entirely or partially exchanged for an equivalent quantity of a heavy metal, whilst the negative group of elements remains unaltered, thus:—

$$K_4FeCy_6 + \mathbf{S}O_2Cuo'' = K_2Cu''FeCy_6 + \mathbf{S}O_2Ko_2, \text{ or}$$
$$K_4FeCy_6 + 2\mathbf{S}O_2Cuo'' = Cu''_2FeCy_6 + 2\mathbf{S}O_2Ko_2.$$

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* Kekulé, Lehrbuch der organischen Chemie, I, p. 314.

On the addition of an alkaline hydrate or carbonate, the whole of the heavy metal is removed as hydrate, with formation of potassic ferrocyanide.

Easily decomposable soluble double cyanides give likewise precipitates with solutions of heavy metals, *e.g.*,

$$2KAgCy_2 + \mathbf{S}O_2Zno'' = \underset{\text{Precipitated.}}{Zn''Ag_2Cy_4} + \mathbf{S}O_2Ko_2;$$

but there is no evidence to show whether these precipitates are real compounds, or only mixtures of *two* insoluble cyanides; nor is there any proof that alkaline hydrates reproduce the original double cyanide. Dilute sulphuric acid decomposes $\mathbf{Zn}Cy_2$ in the above precipitate, AgCy being precipitated; just as if no connection had apparently existed between the two cyanides. Alkaline hydrates or carbonates are without action upon easily decomposable cyanides. A few are decomposed by sulphuretted hydrogen, *e.g.*, K_2CdCy_4, K_2HgCy_4, $KAgCy_2$, with precipitation of a metallic sulphide; in others, such as K_2MnCy_4, K_2NiCy_4, K_2ZnCy_4, and K_2CuCy_4, the metal is only partially precipitated as sulphide, whilst $K_4Fe''Cy_6$ and $K_4Co''Cy_6$ are not precipitated at all.

It is evident from these changes that easily decomposable and difficultly decomposable double cyanides (ferro-, ferri-, cobalti-, and chromi-cyanides) differ not so much in their chemical structure and habitus, as in the degree of stability which they exhibit.

We employ A SOLUTION OF POTASSIC CYANIDE, KCy.

$\mathbf{N}O_2Ago$ gives a *white curdy* precipitate[*] of **argentic cyanide**, AgCy, insoluble in dilute nitric acid; soluble in ammonic hydrate, sodic hyposulphite, and potassic cyanide. The precipitate resembles AgCl so very closely that special experiments are required to distinguish it from the latter, or to detect hydrocyanic acid in the presence of a chloride.

On igniting a mixture of AgCl and AgCy, which has been entirely freed from argentic nitrate by washing with hot water, AgCy is decomposed into cyanogen, metallic silver, and paracyanogen. AgCl, on the other hand, fuses without decomposition. On dissolving the residue in nitric acid and filtering, a precipitate of AgCl is obtained on the addition of hydrochloric acid or of a soluble chloride, the silver of which must have been present originally as cyanide.

Dilute mineral acids decompose potassic cyanide with evolution of HCy. On decomposing, therefore, a small quantity of KCy by dilute sulphuric acid, in a small porcelain dish, and inverting another small dish, containing a drop or two of yellow ammonic sulphide, over it, the gaseous hydrocyanic acid, acting upon the ammonic sulphide, forms ammonic sulphocyanate, CyAms, and

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[*] $\mathbf{Hg}Cy_2$ is not precipitated by argentic nitrate.

AmHs, thus:—

$$\mathbf{S}_2Am_2 + HCy = CyAms + AmHs,$$

which gives, on acidulating with hydrochloric acid, a characteristic *blood-red coloration* with $\mathbf{Fe}_2Cl_6$.

This constitutes one of the most delicate reactions for free hydrocyanic acid, as well as for soluble or easily decomposable cyanides.

$\mathbf{S}O_2Cuo''$, to which a solution of $\mathbf{S}OHo_2$ has been added, gives with KCy a *white* precipitate of **cuprous cyanide**, $'\mathbf{Cu}'_2Cy_2$, soluble in potassic cyanide ($K_2{}'Cu'_2Cy_4$).

$\mathbf{N}_2O_4Hg_2o''$ gives a *grey* precipitate of metallic mercury, whilst $\mathbf{Hg}Cy_2$ remains in solution, thus:—

$$'\mathbf{Hg}'_2Cy_2 = Hg + \mathbf{Hg}Cy_2.$$

Iron salts are among the most delicate reagents for hydrocyanic acid or for soluble cyanides, on account of their tendency, especially in the presence of potassic hydrate, to form difficultly decomposable double cyanides, containing the compound acid radicals ferro- and ferri-cyanogen, which are of a characteristic blue colour. (Hence the name cyanogen from *κύανος*, blue, and *γεννάω*, I generate.) The solution containing hydrocyanic acid or a soluble cyanide is first treated with a little potassic hydrate, then with a mixture of a ferrous and ferric salt (obtained by exposing a solution of ferrous sulphate for some time to the air) and heated. On the addition of dilute hydrochloric acid, in order to dissolve the $\mathbf{Fe}Ho_2$ and $\mathbf{Fe}_2Ho_6$, which are likewise precipitated by potassic hydrate, a fine blue precipitate of Prussian blue is obtained. The changes may be expressed by the equations:—

$$(1)\ KHo + HCy = KCy + \mathbf{O}H_2.$$

$$(2)\ \mathbf{S}O_2Feo'' + 2KCy = \mathbf{Fe}''Cy_2{}^{*} + \mathbf{S}O_2Ko_2.$$

$\mathbf{Fe}Cy_2$, by combining with 4KCy, forms the soluble double cyanide K_4FeCy_6.

$$(3)\ \mathbf{S}_3O_6Fe_2o^{vi} + 3K_4FeCy_6 = 3Fe''Cy_2,2'Fe'''_2Cy_6 + 6\mathbf{S}O_2Ko_2.$$

Free hydrocyanic acid dissolves mercuric oxide, with formation of mercuric cyanide which is not precipitated by alkalies.

The alkali salts of the compound cyanogen radicals, $FeCy_6$, Fe_2Cy_{12}, Co_2Cy_{12}, are decomposed by moderately concentrated sulphuric acid with evolution of hydrocyanic acid.

This furnishes us with a convenient method for preparing hydrocyanic acid. Ten parts by weight of K_4FeCy_6 (yellow prussiate of potash) are distilled in a flask or retort with 36 to 40 parts of dilute sulphuric acid (one of acid to six of water). The flask or retort is connected with a Liebig's condenser and double-necked receiver from which any uncondensed gas can be carried under a Bunsen lamp. Every joint should be made perfectly tight, and the con-

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[*] $\mathbf{Fe}Cy_2$ is difficultly obtained in an isolated condition, as it forms, in the presence of KCy, potassic ferrocyanide, K_4FeCy_6, containing the compound cyanogen radical $FeCy_6$.

denser-tube should dip into the water placed in the receiver. The reaction takes place according to the equation:—

$$2K_4FeCy_6 + 3\mathbf{S}O_2Ho_2 = 6HCy + \underset{\text{White residue turning blue by exposure to the atmosphere.}}{K_2Fe''FeCy_6} + 3\mathbf{S}O_2Ko_2.$$

Hydrocyanic acid is exceedingly poisonous. Small quantities of the gaseous acid, when inhaled, cause a peculiar sensation in the throat and are followed by headache, giddiness, and other disagreeable symptoms. (Antidotes: ammonia gas or chlorine.) Great care must therefore be taken in operating with HCy or with cyanogen compounds generally, and for the purposes of analysis small quantities only should be operated upon at a time.

HYDROFERROCYANIC ACID, H_4FeCy_6.—This acid is *tetrabasic*, *i.e.*, its four hydrogen atoms can be replaced by four atoms of a monad or two atoms of a dyad metal. The potassium salt is prepared on a manufacturing scale by introducing nitrogenous animal substances (horn-shavings, etc.) and iron into fused wood-ashes. The fused mass is lixiviated with water and the salt allowed to crystallise out. It may also be prepared by decomposing Prussian blue with KHo or $\mathbf{C}OKo_2$ and separating the ferric hydrate by filtration, thus:—

$$3Fe''Cy_2,2'Fe'''_2Cy_6 + 12KHo = 3K_4FeCy_6 + 2\mathbf{Fe}_2Ho_6.$$

Potassic ferrocyanide, $K_4FeCy_6 + 3Aq$, crystallises in large lemon-yellow crystals; hence its name *yellow prussiate of potash.* Its positive element (potassium) can, by double decomposition, be replaced by other metals, either entirely or partially, and the property of cyanogen to form double cyanides is well illustrated by the deportment of the more complex ferrocyanides. This will be seen from the following list of some of the more common ferrocyanides:—

$K_4FeCy_6 + 3Aq.$
$Na_4FeCy_6 + 6Aq.$
$Am_4FeCy_6 + 3Aq.$
$Ba''_2FeCy_6 + 6Aq.$
$K_2Ba''FeCy_6 + 3Aq.$
$Ca''_2FeCy_6 + 12Aq.$
$K_2Ca''FeCy_6 + 3Aq.$
$Cu_2FeCy_6 + 4Aq.$
$K_2Cu''FeCy_6 + 2Aq.$
$K_2Fe''FeCy_6.$
$NaK_3FeCy_6 + 3Aq.$
$AmK_3FeCy_6 + 3Aq.$

REACTIONS IN THE DRY WAY.

K_4FeCy_6 fuses, when strongly ignited, and breaks up into nitrogen, potassic cyanide, and carbide of iron, or a mixture of carbon and iron; thus:—

$$K_4FeCy_6 = 4KCy + C_2Fe + N_2.$$

Heated with free access of air, or in contact with metallic oxides, the KCy is further converted into potassic cyanate, CyKo.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF POTASSIC FERROCYANIDE.

The alkaline ferrocyanides are readily soluble in water, the alkaline earthy ferrocyanides are difficultly soluble; those of iron and most other metals are insoluble in water, and many of them also insoluble in acids. They are decomposed on boiling with potassic hydrate with formation of a solution of potassic ferrocyanide, and an insoluble metallic hydrate. Some ferrocyanides are remarkable for their characteristic colour, notably so those of iron and copper; others are white, *e.g.*, those of the alkaline earthy metals, of Zn, Pb, Ag, Hg; greenish white, *e.g.*, Ni''_2FeCy_6, $Co_2''FeCy_6$; reddish white, *e.g.*, Mn''_2FeCy_6. Potassic ferrocyanide is employed, on this account, as a useful reagent in the qualitative examination of metals, especially of iron and copper.

$\mathbf{N}O_2Ago$ produces a *white* precipitate of **argentic ferrocyanide**, Ag_4FeCy_6, insoluble in dilute nitric acid and ammonic hydrate, soluble in potassic cyanide.

$\mathbf{S}O_2Cuo''$, added in excess, gives with a solution of K_4FeCy_6 a *red* (*chocolate-coloured*) precipitate of **dicupric ferrocyanide**, Cu''_2FeCy_6, whilst an insufficient amount of the cupric salt gives a *brown* precipitate of **dipotassic cupric ferrocyanide**, $K_2Cu''FeCy_6$.

$\mathbf{S}O_2Feo''$ gives a *light blue* precipitate of **dipotassic ferrous ferrocyanide**, $K_2Fe''FeCy_6$, thus:—

$$K_4FeCy_6 + \mathbf{S}O_2Feo'' = K_2Fe''FeCy_6 + \mathbf{S}O_2Ko_2,$$

which is slowly *oxidized* by exposure to the air, or rapidly, by oxidizing agents, such as nitric acid or chlorine water: a part of the potassium being removed as oxide, or chloride, thus:—

$$\underset{\substack{\text{Light blue}\\\text{precipitate.}}}{2Fe''K_2FeCy_6} + Cl_2 = \underset{\substack{\text{Diferrous dipotassic}\\\text{ferricyanide.}}}{Fe''_2K_2Fe_2Cy_{12}} + 2KCl,$$

or potassic ferricyanide in which four atoms of potassium have been replaced by two atoms of dyad iron.

Potassic ferrocyanide is in fact readily converted into potassic ferricyanide, $K_6Fe_2Cy_{12}$ (analogous to the conversion of ferrous salts into ferric salts), by various oxidizing agents, such as chlorine, nitric acid, potassic chlorate and hydrochloric acid, etc.

$\mathbf{Fe}_2Cl_6$ gives an *intensely blue* precipitate of $3Fe''Cy_2, 2'Fe'''_2Cy_6$ called **Prussian blue**, thus:—

$$3K_4FeCy_6 + \mathbf{Fe}_2Cl_6 = 3Fe''Cy_2,2'Fe'''_2Cy_6 + 12KCl,$$

which constitutes at once a most characteristic and delicate reaction for ferric salts and for ferrocyanogen (as well as for cyanogen, as has been already shown). This precipitate is insoluble in dilute mineral acids, but dissolves in oxalic acid to a blue liquid (blue ink), and in ammonic tartrate to a violet liquid. It is decomposed by alkalies. On boiling with mercuric oxide, Prussian blue is entirely decomposed into $\mathbf{Hg}Cy_2$ and ferrous and ferric oxides, thus:—

$$3Fe''Cy_2,2'Fe'''_2Cy_6 + 9\mathbf{Hg}O = 9\mathbf{Hg}Cy_2 + 3\mathbf{Fe}O + 2\mathbf{Fe}_2O_3.$$

By adding an insufficient amount of $\mathbf{Fe}_2Cl_6$ to a solution of K_4FeCy_6, a blue precipitate is likewise obtained which is, however, soluble in water and is therefore called *soluble Prussian blue* (used for inks). It is generally thought to be composed of one part of Prussian blue and one of potassic ferrocyanide.

Concentrated sulphuric acid (9 parts by weight) decomposes potassic ferrocyanide (1 part by weight) with evolution of carbonic oxide (METHOD FOR PREPARING CARBONIC OXIDE); the nitrogen of the cyanogen being converted into ammonia and left as ammonic sulphate, thus:—

$$K_4FeCy_6 + 6\mathbf{S}O_2Ho_2 + 6\mathbf{O}H_2 = 6CO + 2\mathbf{S}O_2Ko_2 + \mathbf{S}O_2Feo'' + 3\mathbf{S}O_2Amo_2.$$

When concentrated hydrochloric acid is added to an alkaline ferrocyanide, hydroferrocyanic acid separates, in the cold, as a white crystalline powder which turns rapidly blue. If ether be added to the solution of potassic ferrocyanide, previous to its precipitation with concentrated hydrochloric acid, the acid is obtained quite colourless.

HYDROFERRICYANIC ACID, $H_6Fe_2Cy_{12}$.—This acid is *hexabasic*, since its six atoms of basylous hydrogen may be replaced by six atoms of a monad metal, or by three atoms of a dyad metal. Potassic ferricyanide is derived from K_4FeCy_6 by a process of oxidation, as for instance by passing chlorine into an aqueous solution of it, till a solution of ferric chloride produces no longer a blue precipitate, but imparts merely a brown coloration to the liquid. The change is expressed by the equation:—

$$2K_4FeCy_6 + Cl_2 = K_6Fe_2Cy_{12} + 2KCl.$$

It is effected by the abstraction of two atoms of the metal potassium from two parts of K_4FeCy_6. Two atoms of cyanogen are transferred to two molecules of $\mathbf{Fe}Cy_2$, whereby the ferrous cyanide is converted into ferric cyanide, thus:—

$$2(4KCy,FeCy_2) = 6KCy,'Fe'''_2Cy_6 + K_2.$$

It is also called *red prussiate of potash* on account of the dark red-coloured crystals which are separated from potassic chloride by crystallisation.

Reducing agents convert it into potassic ferrocyanide, especially in alkaline solutions. The transformation is effected by the addition of two atoms of the metal potassium:—

$$K_6Fe_2Cy_{12} + K_2 = 2K_4FeCy_6.$$

The ferric cyanide in the double cyanide is reduced to ferrous cyanide, thus:—

$$6KCy,'Fe'''_2Cy_6 + K_2 = 8KCy,2Fe''Cy_2, \text{ or } 2(4KCy,FeCy_2) = 2K_4FeCy_6.$$

The following are instances of indirect oxidation effected by potassic ferricyanide:—

$\mathbf{S}H_2$ converts the ferri- into a ferrocyanide, with separation of sulphur,
KI " " " with precipitation of iodine,
$\mathbf{Cr}_2O_3$, or its salts, in the presence of KHo is converted into $\mathbf{Cr}O_3$,
$\mathbf{Pb}O$ " " " " $\mathbf{Pb}O_2$,
$\mathbf{Mn}O$ " " " " $\mathbf{Mn}O_2$,
$\mathbf{Sn}O$ " " " " $\mathbf{Sn}O_2$,
$\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right.$ " " " $\mathbf{C}O_2$,
KCy " " " CyKo,
$\mathbf{P}_2O_3$ " " " $\mathbf{P}_2O_5$,
$\mathbf{S}O_2$ " " " $\mathbf{S}O_3$,

$\mathbf{N}H_3$ gives with $K_6Fe_2Cy_{12}$ potassic and ammonic ferrocyanides with evolution of nitrogen gas, thus:—

$$6K_6Fe_2Cy_{12} + 16\mathbf{N}H_3 = 9K_4FeCy_6 + 3Am_4FeCy_6 + N_4.$$

Many organic substances, *e.g.*, sugar, dextrine, starch, alcohol, and even paper, are oxidized, in the presence of an alkali, to $\mathbf{C}O_2$ and $\mathbf{O}H_2$. Indigo is bleached. Phosphorus, sulphur, and iodine are converted by the action of $K_6Fe_2Cy_{12}$, in the presence of alkalies, into $\mathbf{S}O_2Ho_2$, $\mathbf{P}OHo_3$, $\left\{\begin{matrix}OI\\ OHo\end{matrix}\right.$. Analogous to potassic ferrocyanide it forms *double ferricyanides*, by the partial or entire replacement of the six atoms of the positive element, potassium, by different metals. The following are some of the more important metallic ferricyanides:—

$K_6Fe_2Cy_{12}$.
$Na_6Fe_2Cy_{12}$ + Aq.
$Ca''_3Fe_2Cy_{12}$ + 6Aq.
$Ba''_2K_2Fe_2Cy_{12}$ + 3Aq.
$Fe''_3Fe_2Cy_{12}$ (Turnbull's blue).

REACTIONS IN THE DRY WAY.

Potassic ferricyanide is decomposed upon ignition, yielding cyanogen and nitrogen, and leaving a residue, consisting of potassic cyanide, potassic ferrocyanide, Prussian blue, paracyanogen, carbon and iron.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF POTASSIC FERRICYANIDE.

The alkaline ferricyanides are readily soluble in water. The others are mostly insoluble.

$\mathbf{N}O_2Ago$ produces an *orange coloured* precipitate of **argentic ferricyanide**, $Ag_6Fe_2Cy_{12}$, insoluble in dilute nitric acid, but readily soluble in ammonic hydrate and potassic cyanide.

$\mathbf{S}O_2Feo''$ gives a *blue* precipitate (*Turnbull's blue*) of $Fe''_3Fe_2Cy_{12}$,

triferrous ferricyanide, which is decomposed by potassic hydrate into potassic ferrocyanide and ferrous and ferric hydrates:

$$Fe''_3Fe_2Cy_{12} + 8KHo = 2K_4FeCy_6 + \mathbf{Fe}''Ho_2 + \mathbf{Fe}_2Ho_6.$$

$\mathbf{Fe}_2Cl_6$ produces no precipitate, but gives a *brownish coloration. The deportment of potassic ferro- and ferricyanide with iron salts enables us to distinguish between ferrous and ferric salts.*

HYDROCOBALTICYANIC ACID, $H_6Co'''_2Cy_{12}$.—Solutions of cobaltous salts are precipitated by KCy. The precipitate consists of flesh-coloured or cinnamon-brown cobaltous cyanide, $\mathbf{Co}Cy_2$. Excess of potassic cyanide dissolves the precipitate, forming a readily decomposable double cyanide, which, on boiling, or on the addition of HCl, is converted into a difficultly decomposable double cyanide, analogous to potassic ferricyanide, with evolution of hydrogen, thus:—

$$2(4KCy,CoCy_2) + 2\mathbf{O}H_2 = K_6Co_2Cy_{12} + 2KHo + H_2.$$

Potassic cobalticyanide.

This double cyanide is of great interest, because *it enables us to separate cobalt from nickel, both qualitatively and quantitatively.*

CYANIC ACID, CyHo.—Obtained in the form of potassic cyanate by the oxidation of KCy or K_4FeCy_6. This salt is very stable when heated by itself, but deliquesces in the air, and is broken up by water into an acid carbonate and ammonia, thus:—

$$CyKo + 2\mathbf{O}H_2 = \mathbf{C}OHoKo + \mathbf{N}H_3.$$

Potassic cyanate is invariably found in commercial potassic cyanide, sometimes to a considerable extent.

REACTIONS IN THE DRY WAY.

It acts as a flux in blowpipe reactions, and is a powerful *oxidizing* agent. When heated with charcoal, it is converted into KCy, CO and $\mathbf{C}O_2$. On heating, therefore, a metallic oxide on charcoal, with KCy containing CyKo, the oxide is reduced to the metallic state.

REACTIONS IN THE WET WAY.

The cyanates of the alkalies, alkaline earths, and a few metallic oxides are soluble in water, but decompose rapidly with evolution of ammonia. $\mathbf{N}O_2Ago$ produces with potassic cyanate a *white* precipitate of **argentic cyanate**, CyAgo, *soluble* in ammonic hydrate, and in dilute nitric acid; AgCy is *insoluble* in nitric acid.

Moderately concentrated sulphuric or hydrochloric acid decomposes CyKo with effervescence, owing to the liberation of CyHo, which affects the eyes most painfully and is recognized by its pungent odour, resembling that of strong acetic acid; the greater portion of the liberated acid is, however, decomposed at once by water into $\mathbf{C}O_2$, and an ammonic salt, thus:—

$$2CyKo + 2\mathbf{S}O_2Ho_2 + 2\mathbf{O}H_2 = 2\mathbf{C}O_2 + \mathbf{S}O_2Ko_2 + \mathbf{S}O_2Amo_2.$$

SULPHOCYANIC ACID, CyHs.—Obtained in combination with potassium by heating KCy with sulphur or a metallic sulphide. Hence its use for *reducing* metallic sulphides in blowpipe reactions.

REACTIONS IN THE DRY WAY.

CyKs can be fused out of contact with the air, without undergoing decomposition. It turns first brown, then green, and lastly indigo blue, but becomes again colourless on cooling. In contact with the air, CyKs is converted into cyanate and sulphate, with disengagement of $\mathbf{S}O_2$. The sulphocyanates of the heavy metals are decomposed upon ignition, $\mathbf{C}S_2$ being given off at first, and on raising the temperature a mixture of nitrogen and cyanogen is evolved, whilst a metallic sulphide is left :—

$$4\genfrac{}{}{0pt}{}{Cy}{Cy}Cus'' = N_2 + 3\left\{\begin{matrix}\mathbf{C}N\\ \mathbf{C}N\end{matrix}\right. + 2\mathbf{C}S_2 + 4\mathbf{Cu}S.$$

REACTIONS IN THE WET WAY.

We employ a SOLUTION OF AMMONIC SULPHOCYANATE, CyAms.

$\mathbf{N}O_2Ago$ produces a *white curdy* precipitate of **argentic sulphocyanate,** CyAgs, insoluble in water and in dilute acids ; it is soluble in ammonic hydrate, from which it crystallises out on evaporation. It is also soluble in CyAms or CyKs, forming a double sulphocyanate (CyAgs, CyKs), from which water or hydrochloric acid precipitates granular—ammonic hydrate crystalline CyAgs.

$\mathbf{S}O_2Cuo''$ gives a *black* crystalline precipitate of **cupric sulphocyanate,** $\genfrac{}{}{0pt}{}{Cy}{Cy}Cus''$ which on standing in the liquid is converted into **cuprous sulphocyanate,** $\genfrac{}{}{0pt}{}{Cy}{Cy}Cu_2s''$. This characteristic cuprous salt is obtained instantly by adding $\mathbf{S}OHo_2$, or a solution of a ferrous salt to the cupric salt.

$\mathbf{Fe}_2Cl_6$ produces an *intensely red solution*, owing to the formation of a soluble **ferric sulphocyanate,** $Cy_6Fe_2s^{vi}$. Alkaline sulphocyanates furnish us, on this account, with a *most delicate reaction for ferric salts.* This reaction serves also for the detection of sulphocyanogen and hydrocyanic acid. The blood red colour is destroyed by $\mathbf{Hg}Cl_2$. On introducing some metallic zinc into the blood red solution, $\mathbf{S}H_2$, is evolved.

QUESTIONS AND EXERCISES.

1. Explain the derivation of the term cyanogen.
2. Why are $\left\{\begin{matrix}\mathbf{C}N\\ \mathbf{C}N\end{matrix}\right.$, $\mathbf{Fe}Cy_6$ and $\mathbf{Fe}_2Cy_{12}$ viewed as compound radicals?
3. How are KCy, K_4FeCy_6 and $K_6Fe_2Cy_{12}$ prepared? Describe their properties, as far as the analytical data illustrate them.
4. Explain the action of heat upon KCy and K_4FeCy_6, 1st, out of contact with air ; 2nd, with free access of air.
5. What constitutes the usefulness of KCy as a reagent for blowpipe experiments?
6. Explain the changes which cyanides of the heavy metals undergo upon ignition.
7. How would you prepare cyanogen gas? Describe its properties.
8. Classify cyanides according to their solubility in water. Enumerate some of the more important single cyanides.
9. What is understood by soluble double cyanides? How are they classified, and how can the easily decomposable double cyanides be distinguished, from the difficultly decomposable double cyanides?
10. Enumerate, 1st, easily decomposable double cyanides ; 2nd, difficultly decomposable double cyanides.
11. Give reasons for the existence of the compound radicals ferro-, ferri- and

cobalticyanogen in the double cyanides $\mathrm{K_4FeCy_6}$, $\mathrm{Pb''''_2Fe_2Cy_{12}}$, $\mathrm{Cu''_3Co_2Cy_{12}}$.

12. Explain the action of dilute acids upon single cyanides and upon easily decomposable double cyanides.
13. Explain the difference between a precipitate, produced by a solution of a salt of a heavy metal with a solution of an easily decomposable double cyanide, or with an alkaline ferro- or ferricyanide.
14. What is the action of hydrated and carbonated alkalies upon the two classes of double cyanides?
15. Explain the action of $\mathbf{S}\mathrm{H_2}$ upon the following cyanides and double cyanides: $\mathbf{Hg}\mathrm{Cy_2}$, $\mathrm{K_2CdCy_4}$, $\mathrm{KAgCy_2}$, $\mathrm{K_2MnCy_4}$, $\mathrm{K_2CuCy_4}$, $\mathrm{K_2CoCy_4}$, $\mathrm{K_2NiCy_4}$.
16. How is AgCy distinguished from AgCl?
17. Describe the action of HCy upon $\mathbf{S}_2\mathrm{Am_2}$, and explain how traces of HCy can be detected, in the presence of ferro- or ferricyanogen compounds.
18. How would you demonstrate the greater stability of $\mathbf{Hg}\mathrm{Cl_2}$ over that of $\mathbf{Hg}\mathrm{Cy_2}$?
19. Explain the use of ferroso-ferric salts for the detection of HCy.
20. How is HCy prepared? Describe its properties.
21. Describe shortly how yellow prussiate of potash can be prepared.
22. Enumerate some of the more common ferrocyanides.
23. How would you examine a ferrocyanide insoluble in acids, *e.g.*, *Prussian blue?*
24. Explain the action of KHo upon *Prussian blue* and upon *Turnbull's blue*.
25. Explain what reactions ferrous and ferric salts give with ferro- and ferricyanides.
26. Explain the formation of soluble Prussian blue.
27. What is the action of dilute or of concentrated sulphuric acid upon potassic ferrocyanide?
28. State how $\mathrm{H_4FeCy_6}$ is prepared.
29. Explain the conversion of potassic ferro- into ferricyanide.
30. Give instances of the oxidizing action of potassic ferricyanide in alkaline solutions.
31. Enumerate some of the more important metallic ferricyanides.
32. How can argentic ferro- and ferricyanides be separated from each other?
33. What decomposition takes place when ferro- and ferricyanides are fused with a mixture of ammonic sulphate and nitrate?
34. How is CyHo recognized in the presence of a cyanide?
35. What is the action of concentrated $\mathbf{S}\mathrm{O_2Ho_2}$ upon a cyanate?
36. What reactions take place when potassic cyanate is heated with charcoal, with $\mathbf{Mn}\mathrm{O_2}$ or with $\mathbf{O}\mathrm{H_2}$?
37. Explain the formation of potassic sulphocyanate and state what change it undergoes when heated in contact with air.
38. Explain the action of nascent hydrogen upon ferric sulphocyanate.
39. Why does potassic sulphocyanate enable us to distinguish between ferrous and ferric salts?
40. Calculate the percentage composition of cuprous sulphocyanate, ${}^{\mathrm{Cy}}_{\mathrm{Cy}}\mathrm{Cu_2s''}$.

CHAPTER VIII.

REACTIONS OF THE ACIDS.

B. ORGANIC ACIDS.

MOST organic acids cannot be distinguished qualitatively as readily as inorganic acids. A few of the more generally occurring acids which can be readily detected, claim a short notice.

The greater number of organic acids consist of carbon, hydrogen and oxygen; some also contain nitrogen. There is no organic acid known containing only two single atoms of an element, and only one containing three, viz., hydrocyanic acid, HCN; whilst the number of atoms in a molecule of an organic acid, as for instance in stearic acid, $\mathbf{C}_{18}H_{36}O_2$, is far greater than in any inorganic compound.

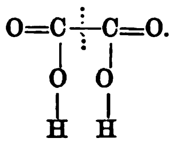
The element with which oxygen, hydrogen and nitrogen are grouped in organic acids is *carbon* which in most cases, probably in all, acts as a *tetrad* element.*

Groups of elements performing similar functions in organic acids, and built up invariably in the same manner, are called *compound organic radicals.*

Nearly every organic acid contains one acidifying principle of two negative compound radicals, *e.g.*:—

Cyanogen (molecule) $\left\{\begin{matrix}\mathbf{C}\mathrm{N}''' \\ \mathbf{C}\mathrm{N}'''\end{matrix}\right.$ $\mathrm{N{\equiv}C}\vdots\mathrm{C{\equiv}N}$, or

Oxatyl (the molecule of which is dry oxalic acid) $\left\{\begin{matrix}\mathbf{C}\mathrm{OHo} \\ \mathbf{C}\mathrm{OHo}\end{matrix}\right.$



$$\begin{matrix}\mathrm{O{=}C} & \vdots & \mathrm{C{=}O.} \\ | & & | \\ \mathrm{O} & & \mathrm{O} \\ | & & | \\ \mathrm{H} & & \mathrm{H}\end{matrix}$$

The semimolecule of each of these compound radicals contains one atom of carbon with one bond left free to combine with another element, or group of elements, the other three bonds being satisfied, in cyanogen, by combining with triad nitrogen, or in oxatyl, with one atom of oxygen and one of hydroxyl. In the molecules the two free bonds of the carbon satisfy each other.

These radicals are closely related to each other. An aqueous solution of cyanogen (one volume of water dissolves about four volumes of the gas) is speedily transformed into ammonic oxalate, thus:—

$$\left\{\begin{matrix}\mathbf{C}\mathrm{N} \\ \mathbf{C}\mathrm{N}\end{matrix}\right. + 4\mathbf{O}\mathrm{H}_2 = \left\{\begin{matrix}\mathbf{C}\mathrm{OAmo} \\ \mathbf{C}\mathrm{OAmo}\end{matrix}\right..$$

In the presence of a boiling solution of potassic hydrate, cyanogen evolves ammonia and produces potassic oxalate, thus:—

$$\left\{\begin{matrix}\mathbf{C}\mathrm{N}''' \\ \mathbf{C}\mathrm{N}'''\end{matrix}\right. + 2\mathrm{KHo} + 2\mathbf{O}\mathrm{H}_2 = \left\{\begin{matrix}\mathbf{C}\mathrm{OKo} \\ \mathbf{C}\mathrm{OKo}\end{matrix}\right. + 2\mathbf{N}\mathrm{H}_3.$$

from which salt oxalic acid can be obtained.

Oxalic acid, on the other hand, may be converted into cyanogen, by transforming it into ammonic oxalate and submitting this salt to the action of heat, thus:—

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* Frankland: Lecture Notes, page 199.

$$\left\{\begin{array}{l}\mathbf{C}\mathrm{O(NH_4O)}\\ \mathbf{C}\mathrm{O(NH_4O)}\end{array}\right. = \left\{\begin{array}{l}\mathbf{C}\mathrm{N'''}\\ \mathbf{C}\mathrm{N'''}\end{array}\right. + 4\mathbf{O}\mathrm{H_2}.$$

Oxalic acid, or the molecule of the compound radical oxatyl, results from the oxidation of a large number of organic bodies, *e.g.*, sugar, woody fibre, etc., by the action of powerful oxidizing agents, such as concentrated nitric acid, and is resolved into the two products of the final oxidation of everything organic, viz., carbonic anhydride and water.

Heat, in fact, breaks up nearly all salts of organic acids. Those of alkaline and alkaline earthy bases, leave upon gentle ignition *carbonates*, with separation of *carbon*, and consequent blackening, oxalates excepted. The carbonaceous residue being soluble in water, indicates that the organic acid was combined with alkali metals, and if insoluble, with alkaline earthy bases. The decomposition is, moreover, accompanied in most instances by the evolution of volatile matter, of carbonic oxide and hydrocarbons, empyreumatic vapours and oils.

In the free state organic acids are either *volatile*, and can be distilled or sublimed, generally without undergoing decomposition and without leaving any carbonaceous residue, as for instance, formic acid, and its homologues acetic acid, etc. (or the acids of the fatty acid series); benzoic acid and others, belonging to the series of aromatic organic acids. These acids can be removed from any of their saline compounds by decomposition with dilute sulphuric acid. Other organic acids are *non-volatile*, and are decomposed when heated by themselves, leaving a carbonaceous residue; and the acids cannot be removed from their salts by distillation with sulphuric acid.

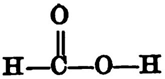
FORMIC ACID, $\left\{\begin{array}{l}\mathrm{H}\\ \mathbf{C}\mathrm{OHo}\end{array}\right.$.—Obtained in a great many chemical reactions, as a product of oxidation or decomposition. It is usually prepared by heating a mixture of equal weights of crystallised oxalic acid and glycerine to 75° C., and distilling with water—

$$\left\{\begin{array}{l}\mathbf{C}\mathrm{OHo}\\ \mathbf{C}\mathrm{OHo}\end{array}\right. = \left\{\begin{array}{l}\mathrm{H}\\ \mathbf{C}\mathrm{OHo}\end{array}\right. + \mathbf{C}\mathrm{O_2}.$$

Formic acid distils at 100° C. It is of interest as being the lowest possible acid in the series of fatty acids, a series which most comprehensively illustrates the structure of organic acids.

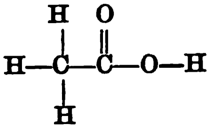
By a successive increment of $\mathbf{C}\mathrm{H_2}$, or by substituting for H—the positive element in formic acid—successively semi-molecules of the compound organic radicals methyl, $\mathbf{C}\mathrm{H_3}$, ethyl, $\mathbf{C}_2\mathrm{H_5}$, etc., the whole series of fatty acids can be obtained, thus:—

Formic acid $\left\{\begin{array}{l}H\\ \mathbf{C}OHo\end{array}\right.$



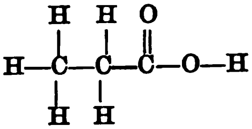
$H-\overset{\overset{O}{\|}}{C}-O-H$

Acetic acid $\left\{\begin{array}{l}H\\ \mathbf{C}H_2\\ \mathbf{C}OHo\end{array}\right.$ or $\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}OHo\end{array}\right.$



$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-O-H$

Propionic acid $\left\{\begin{array}{l}H\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}OHo\end{array}\right.$ or $\left\{\begin{array}{l}\mathbf{C}_2H_5\\ \mathbf{C}OHo\end{array}\right.$



$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-O-H$

Butyric acid $\left\{\begin{array}{l}H\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}OHo\end{array}\right.$ or $\left\{\begin{array}{l}\mathbf{C}_3H_7\\ \mathbf{C}OHo\end{array}\right.$

Stearic acid $\left\{\begin{array}{l}H\\ (\mathbf{C}H_2)_{17}\\ \mathbf{C}OHo\end{array}\right.$ or $\left\{\begin{array}{l}\mathbf{C}_{17}H_{35}\\ \mathbf{C}OHo\end{array}\right.$

The lower members of the series of fatty acids dissolve freely in water, whilst the more complex fatty acids, with largely increased molecular weights—to mention only stearic acid—are quite insoluble in water.

REACTIONS IN THE DRY WAY.

Formates of the fixed alkalies and alkaline earthy bases, when heated out of contact with air, are decomposed into carbonates and a little carbon, with disengagement of combustible gases—mainly carbonic oxide and hydrogen. Formates of the heavy metals give off $\mathbf{C}O_2$, CO, and $\mathbf{O}H_2$, leaving the metal (generally mixed with a little carbon).

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF SODIC FORMATE, $\left\{\begin{array}{l}H\\ \mathbf{C}ONao\end{array}\right.$.

All formates are soluble in water; some also in alcohol.

Formic acid and formates are readily recognized by their property of reducing salts of the noble metals, *e.g.*, $\mathbf{Au}Cl_3$, $\mathbf{N}O_2Ago$, $\mathbf{N}_2O_4Hg_2o''$, or $\mathbf{Hg}Cl_2$ to the metallic state, with evolution of carbonic anhydride.

Potassic permanganate is likewise deoxidized by formic acid.

This *reducing action distinguishes formic acid from acetic acid and most of its homologues.*

When heated with concentrated sulphuric acid, formic acid and formates are broken up into water and carbonic oxide, which latter burns with a fine blue flame. (METHOD OF PREPARING CARBONIC OXIDE GAS.) The mixture does not blacken. The decomposition is expressed thus:—

$$\left\{\begin{matrix}H\\ \mathbf{C}OHo\end{matrix}\right. + \mathbf{S}O_2Ho_2 = CO + \mathbf{S}O_2Ho_2 + \mathbf{O}H_2.$$

ACETIC ACID (Vinegar), $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$.—Obtained either by the oxidation of alcohol, thus:—

$$\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}H_2Ho\end{matrix}\right. + O_2 = \left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right. + \mathbf{O}H_2,$$

or by the destructive distillation of vegetable substances, especially of wood. Pure acetic acid boils at 117° C., and is prepared by decomposing dry sodic acetate (5 parts by weight) with concentrated sulphuric acid (6 parts by weight). The crude acid is placed over $\mathbf{Mn}O_2$, in order to destroy any $\mathbf{S}O_2$, and rectified by distillation over a little sodic acetate.

REACTIONS IN THE DRY WAY.

Acetates are decomposed upon ignition, yielding a peculiar inflammable volatile liquid called *acetone*, $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}O\mathbf{C}H_3\end{matrix}\right.$, thus:—

$$2\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}ONao\end{matrix}\right. = \mathbf{C}ONao_2 + \left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}O\mathbf{C}H_3.\end{matrix}\right.$$

The acetates of the alkalies and alkaline earthy bases, when strongly ignited, leave a carbonate; those of the heavy metals leave either a metallic oxide, or the metal itself, mixed with carbon.

Heated with caustic alkalies (soda-lime), as seen in Fig. 89, dry sodic acetate gives off *marsh-gas*, or *light carburetted hydrogen*, $\mathbf{C}H_4$, thus:—

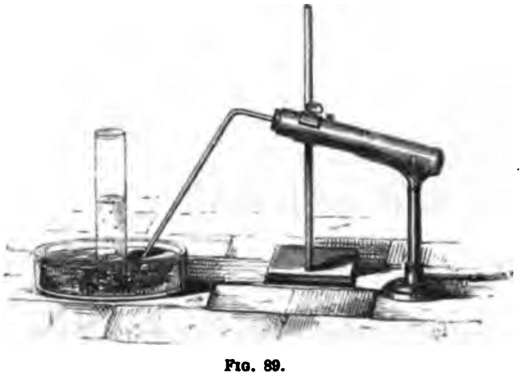


FIG. 89.

$$3\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}ONao\end{matrix}\right. + NaHo,\mathbf{Ca}Ho_2 = 2\mathbf{C}ONao_2,\mathbf{C}OCao'' + 3\mathbf{C}H_4.$$

Marsh-gas.

The gas can be collected in the usual manner over water, and on applying a light it burns with a pale blue flame, with formation of water and carbonic anhydride. It forms one of the constituents of the gas-bubbles which are seen to rise from the bottom of stagnant waters, where decaying organic matter has accumulated. Hence its name *marsh-gas.*

Its specific gravity is ·554 when compared with air. Its molecular weight is 16, one litre weighing 8 criths. It explodes when mixed with air. Light carburetted hydrogen forms a constituent of ordinary coal-gas, and is likewise found in coal mines, where it gives frequently rise to explosions when mixed with air and fired. It is called by the miner *fire-damp*. The atmosphere left in the workings of a coal-pit, after an explosion of fire-damp has taken place, is called *choke-damp*, or *after-damp*, consisting to a large extent of carbonic anhydride.

REACTIONS IN THE WET WAY.

A SOLUTION OF SODIC ACETATE, $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}ONao,\end{matrix}\right.$ may be employed.

All acetates are soluble in water. Argentic and mercurous acetates are the least soluble.

On heating a solid acetate (or a concentrated aqueous solution of it) with alcohol and concentrated sulphuric acid, **acetic ether** (ethylic acetate), $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OEto,\end{matrix}\right.$ (Et=ethyl) is formed which possesses a peculiar fragrant odour. The change is expressed thus:—

$$\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}ONao\end{matrix}\right. + EtHo + \mathbf{S}O_2Ho_2 = \left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OEto\end{matrix}\right. + \mathbf{S}O_2HoNao + \mathbf{O}H_2.$$

Too much alcohol should be avoided lest common (or sulphuric) ether, $\mathbf{O}Et_2$, be formed, the odour of which would mask that of the acetic ether.

By distilling an acetate with moderately dilute sulphuric acid in a retort, free acetic acid is obtained, which is recognized by its characteristic pungent odour.

$\mathbf{Fe}_2Cl_6$ added to a solution of an acetate, produces a deep red-coloured solution, owing to the formation of ferric acetate. On boiling, the whole of the iron is precipitated as **basic ferric acetate,** in the form of *brownish yellow flakes.* AmHo precipitates the iron from a solution of ferric acetate as ferric hydrate.

Ammonic acetate, especially in the presence of ammonia, dissolves several insoluble sulphates, *e.g.*, $\mathbf{S}O_2Pbo''$, $\mathbf{S}O_2Cao''$.

STEARIC ACID, $\left\{\begin{matrix}\mathbf{C}_{17}H_{35}\\ \mathbf{C}OHo\end{matrix}\right.$.—Found in fatty bodies, *e.g.*, pure mutton fat, in combination with glycerine, $\left\{\begin{matrix}\mathbf{C}H_2Ho\\ \mathbf{C}HHo\\ \mathbf{C}H_2Ho\end{matrix}\right.$. When

heated with solutions of caustic alkalies, the fat saponifies and the fatty acid forms with the alkali metal a *soap*, freely soluble in warm water, and the glycerine separates. On decomposing the soap by the addition of an acid (dilute hydrochloric or sulphuric), the fat which separates is found completely changed in character. It has an acid reaction to test-paper when in a melted state, and is soluble with the greatest facility in alcohol from which it crystallises in milky white needles. Its composition is $\mathbf{C}_{18}H_{36}O_2$ or $\left\{\begin{matrix}\mathbf{C}_{17}H_{35}\\ \mathbf{C}OHo\end{matrix}\right.$. It melts at 54°C. Pure hard soap is *sodic stearate*, $\left\{\begin{matrix}\mathbf{C}_{17}H_{35}\\ \mathbf{C}ONao\end{matrix}\right.$, and contains generally—

20 – 25 per cent. of water
7 – 8 „ „ soda ($\mathbf{O}Na_2$)
and 67 – 73 „ „ stearic acid.

The analysis is effected by treating 10 grms. of soap, cut up into thin slices, in a porcelain dish with dilute hydrochloric acid and heating gently for some time, till the whole of the soap is decomposed, the fatty acid floating on the surface. The dish is set aside to cool, when the fatty acid is obtained as a solid cake which can be readily removed and dried between filter paper. Sodic chloride is left in solution and is obtained on evaporation in crystals.

QUESTIONS AND EXERCISES.

1. What elements enter into the composition of organic acids?
2. State which compound organic radicals are met with in organic acids, and show the relation which exists between them.
3. How are the several salts of organic acids influenced by heat, and what inference can be drawn from this action?
4. Explain the structure of the several members of the fatty acid series. Give illustrations.
5. How is formic acid obtained, and what changes do formates undergo, when heated out of contact with air?
6. How can a formate be detected in the wet way? Give equations.
7. State how you would prepare pure carbonic oxide from baric formate.
8. You have given to you plumbic formate, how would you prepare therefrom formic acid and sodic formate?
9. State how acetic acid is prepared.
10. What is the action of heat upon dry acetates?
11. How would you prepare marsh-gas?
12. Explain the terms *fire-damp*, *choke-damp*, or *after-damp*.
13. How can the composition of marsh-gas be shown experimentally?
14. Explain the action of acetic acid upon argentic carbonate or plumbic oxide.
15. What residue is left on igniting sodic acetate, calcic acetate, plumbic acetate, or argentic acetate?
16. Explain how you would obtain acetic ether, describe its composition and properties.
17. Give graphic formulæ for marsh-gas, cyanogen, acetic ether, acetone.
18. Explain the composition of hard soap.
19. A solution containing an unknown quantity of formic acid, when heated with solution of $\mathbf{Au}Cl_3$, yielded 2·235 grms. of metallic gold. How much formic acid by weight did the solution contain?

20. A quantity of crystallised argentic acetate leaves upon ignition 1·236 grm. of metallic silver. How much acetic acid does this correspond to?
21. How much dry sodic acetate must there be decomposed in order to obtain 20 litres of marsh-gas?

BENZOIC ACID, $\left\{\begin{matrix}\mathbf{C}(C_5H_3)H_2\\ \mathbf{C}OHo\end{matrix}\right.$, or shortly $\overline{Bz}Ho$.—Is found in many gums and balsams, from which it is obtained by sublimation. Heated in a tube open at both ends, the acid sublimes in long needles, giving off a very irritating vapour. Heated on platinum foil, benzoic acid burns with a luminous smoky flame.

The crystalline acid is very slightly soluble in water or acids and floats on water. *Benzoates of tetrad metals are mostly insoluble in water, all others are soluble.*

$\mathbf{Fe}_2Cl_6$ gives a *pale yellow* precipitate of **basic ferric benzoate,** $\overline{Bz}_6Fe_2o^{vi},Fe_2O_3+15\ Aq$; and ammonic benzoate is employed sometimes for the separation of Fe^{iv} from Mn'' (compare page 168).

On distilling benzoic acid with lime or baryta, benzol, $\mathbf{C}_6H_6$, is obtained—

$$\left\{\begin{matrix}\mathbf{C}(C_5H_3)H_2\\ \mathbf{C}OHo\end{matrix}\right. + \mathbf{Ca}O + \mathbf{C}_6H_6 + \mathbf{C}OCao''.$$

Dilute acids precipitate benzoic acid from aqueous solutions of benzoates; nitric acid is without action upon it.

Heated with concentrated sulphuric acid, benzoic acid does not blacken, neither does it evolve $\mathbf{S}O_2$.

SUCCINIC ACID, $\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}_2H_4\\ \mathbf{C}OHo\end{matrix}\right.$, or briefly $\overline{Su}Ho_2$—*Dibasic acid.*—Obtained by the distillation of amber, of fossil resin, and also by the long-continued action of nitric acid upon butyric, stearic or margaric acids. The acid crystallises in white plates; is readily soluble in water, alcohol and ether, and is not acted upon by boiling nitric acid. Heated in a tube open at both ends, it sublimes in silky needles. Heated upon platinum foil, it burns with a blue flame and without smoke.

Succinates are decomposed upon ignition, the alkaline and alkaline earthy succinates leave a carbonate, mixed with carbon.

Most succinates are soluble in water.

Plumbic acetate gives a *white* precipitate of **neutral plumbic succinate,** $\left\{\begin{matrix}\mathbf{C}O\\ \mathbf{C}_2H_4\\ \mathbf{C}O\end{matrix}\right. Pbo''$, which is rendered basic by treatment with ammonic hydrate.

$\mathbf{Fe}_2Cl_6$ produces from a solution of neutral ammonic succinate a *brownish red, voluminous* precipitate of **basic ferric succinate,** $\overline{Su}_3Fe_2o^{vi},Fe_2O_3$, readily soluble in mineral acids. AmHo renders the precipitate darker by withdrawing a quantity of succinic acid as ammonic succinate, leaving a more basic succinate. (THIS REACTION SERVES FOR THE SEPARATION OF Mn'' FROM Fe^{iv}.)

On boiling the precipitate, produced by ferric chloride from a solution of a succinate or benzoate, with ammonic hydrate, a soluble ammonic salt of these acids is obtained which can be separated by filtration from the insoluble residue. On the addition of alcohol and $\mathbf{Ba}Cl_2$ to the ammoniacal solution, a *white* precipitate of baric succinate is obtained, whilst benzoic acid gives no precipitate (DISTINCTION BETWEEN $\overline{Bz}Ho$ AND $\overline{Su}Ho_2$).

QUESTIONS AND EXERCISES.

1. How are benzoic and succinic acids prepared? Give graphic formulæ.
2. How would you distinguish $\overline{Bz}Ho$ from $\overline{Su}Ho_2$ in the dry way?
3. State how the precipitate produced by $\overline{Bz}Ho$ and $\overline{Su}Ho_2$ with $\mathbf{Fe}_2Cl_6$ assists us in distinguishing between these two acids.
4. How would you prepare benzol from benzoic acid?
5. You have given to you a mixture of plumbic benzoate and succinate. State how you would obtain the two acids in the free state.
6. 1·340 grm. of the argentic salt of an organic acid leaves upon ignition ·632 grm. of metallic Ag. What is the molecular weight of the acid?

OXALIC ACID, $\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right.$—*Dibasic acid.*—Obtained by the oxidation of a large number of organic bodies, *e.g.*, sugar, by nitric acid; or woody fibre, by the action of caustic alkalies. The free acid, $\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right. + 2Aq$, is a violent poison. It crystallises in rhombic prisms with two molecules of water of crystallisation, which it loses when exposed to dry air, *i.e.*, it effloresces and falls to a powder. With bases it forms an important series of salts called *oxalates*. The acid being dibasic, two series of salts (*neutral* and *acid* oxalates, $\left\{\begin{matrix}\mathbf{C}OKo\\ \mathbf{C}OKo\end{matrix}\right.$ and $\left.\begin{matrix}\mathbf{C}OKo\\ \mathbf{C}OHo\end{matrix}\right)$ exist (besides some *super-acid* oxalates.)

REACTIONS IN THE DRY WAY.

Oxalic acid when heated by itself, sublimes for the most part unchanged; a portion of it breaks up into CO, $\mathbf{C}O_2$ and some formic acid. Oxalates yield, upon ignition, different products of decomposition, according to the nature of the base contained therein.

Alkaline oxalates leave a *carbonate*, with slight blackening, and give off carbonic oxide.

Alkaline earthy oxalates leave a *carbonate*, together with *some caustic base*, if a strong heat be applied, and give off CO and $\mathbf{C}O_2$.

Oxalates containing *metallic bases* which do not form carbonates, or the carbonates of which are decomposed by heat, break up into metallic oxides, and give off equal volumes of CO and $\mathbf{C}O_2$, or into *metal*, as for instance argentic oxalate, giving off $\mathbf{C}O_2$.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF AMMONIC OXALATE, $\left\{\begin{matrix}\mathbf{C}OAmo\\ \mathbf{C}OAmo\end{matrix}\right.$.

Oxalates are either soluble in water, e.g., the alkaline oxalates and a few metallic oxalates; or *insoluble in water, but soluble in acids.*

$\mathbf{Ca}Cl_2$($\mathbf{S}O_2Cao''$ or $\mathbf{Ca}Ho_2$) precipitates even from very dilute solutions *white pulverulent* **calcic oxalate**, $\left\{\begin{matrix}\mathbf{C}O\\ \mathbf{C}O\end{matrix}\right.Cao''$, readily soluble in hydrochloric or nitric acid; almost insoluble in oxalic or acetic acid, and in potassic or ammonic hydrate. Heat promotes the precipitation from very dilute solutions. This constitutes one of the most delicate reactions for oxalic acid.

$\mathbf{Ba}Cl_2$ gives from solutions of neutral oxalates a *white* precipitate of **baric oxalate**, $\left\{\begin{matrix}\mathbf{C}O\\ \mathbf{C}O\end{matrix}\right.Bao'' + Aq$, soluble in oxalic acid, readily soluble in hydrochloric or nitric acid.

$\mathbf{N}O_2Ago$ produces a *white* precipitate of **argentic oxalate**, $\left\{\begin{matrix}\mathbf{C}OAgo\\ \mathbf{C}OAgo\end{matrix}\right.$, soluble in dilute nitric acid and in ammonic hydrate.

Concentrated sulphuric acid decomposes oxalic acid or oxalates, on the application of a gentle heat (Fig. 90), into CO and $\mathbf{C}O_2$,

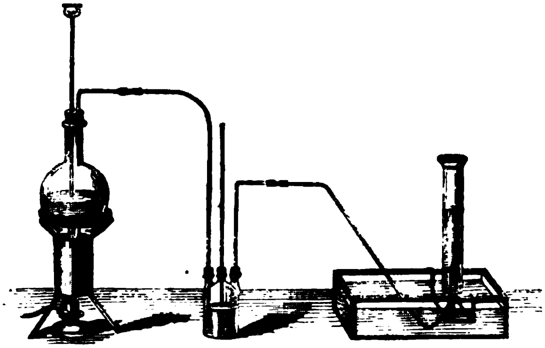


FIG. 90.

without blackening, by withdrawing from the molecule of oxatyl a molecule of $\mathbf{O}H_2$. The gaseous mixture is passed through a wash-bottle containing caustic soda or lime-water, and the carbonic oxide gas is collected over water. The gas burns with a *blue* flame. (USUAL METHOD FOR PREPARING CARBONIC OXIDE.)

Oxalic acid, or oxalates in the presence of free mineral acids, act *as reducing agents.*

$\mathbf{Mn}O_2$ is reduced or deoxidized.—Treat a little black oxide of manganese and oxalic acid or an oxalate with a few drops of concentrated sulphuric acid. Effervescence ensues. The gas which escapes is carbonic anhydride, thus :—

$$\mathbf{Mn}O_2 + \left\{\begin{matrix}\mathbf{C}OKo\\ \mathbf{C}OKo\end{matrix}\right. + 2\mathbf{S}O_2Ho_2 = 2\mathbf{C}O_2 + \mathbf{S}O_2Mno'' + \mathbf{S}O_2Ko_2 + 2\mathbf{O}H_2.$$

A solution of gold, $\mathbf{Au}Cl_3$, is reduced to metallic gold, thus :—

$$2\mathbf{Au}Cl_3 = 3\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right. = 6\mathbf{C}O_2 + Au_2 + 6HCl.$$

Potassic permanganate is speedily reduced (decolorized).

QUESTIONS AND EXERCISES.

1. How is oxalic acid obtained? Describe shortly its properties.
2. What changes does oxalic acid undergo, 1st, upon ignition; 2nd, upon heating with $\mathbf{S}O_2Ho_2$; 3rd, upon treatment with $\mathbf{S}O_2Ho_2$ and $\mathbf{Mn}O_2$ or $\mathbf{Cr}_2O_5Ko_2$; 4th, in contact with $\mathbf{Au}Cl_3$?
3. How would you distinguish calcic oxalate from calcic carbonate, fluoride, borate or phosphate?
4. What takes place when potassic, argentic, calcic or zincic oxalate is ignited by itself?
5. How would you prepare pure carbonic oxide gas from sodic oxalate?
6. Why is oxalic acid decomposed by concentrated sulphuric acid almost without any blackening?
7. Calculate how much $\mathbf{Mn}O_2$ is contained in a sample of black manganic oxide, 2·2 grms. of which, when treated with $\left\{\begin{matrix}\mathbf{C}OKo\\ \mathbf{C}OKo\end{matrix}\right.$ and $\mathbf{S}O_2Ho_2$, yielded 1·662 grm. of $\mathbf{C}O_2$.
8. The calcic salts in one litre of water are precipitated with ammonic oxalate. The precipitate yields upon ignition 1·695 grm. of $\mathbf{C}OCao''$. How much $\mathbf{Ca}O$ does the water contain, 1st, per gallon, 2nd, per 100,000 parts?

TARTARIC ACID, $\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}HHo\\ \mathbf{C}HHo\\ \mathbf{C}OHo\end{matrix}\right.$, shortly $\overline{T}Ho_2$—*Dibasic acid.*—

Found in grapes, tamarinds, pine-apples and several other fruits in the form of hydric potassic tartrate. The acid met with in commerce is prepared from the tartar or *argol*, an impure hydric potassic tartrate, deposited from the grape juice during fermentation. The acid forms colourless transparent crystals, very soluble in water, both hot and cold, and soluble also in alcohol. The aqueous solution undergoes gradual decomposition.

REACTIONS IN THE DRY WAY.

Tartaric acid is decomposed by heat giving off a peculiar *odour*, resembling that of *burnt sugar* (caramel), and leaving a residue of carbon. Alkaline tartrates when heated in a test-tube, are decomposed with evolution of inflammable gases, leaving a mixture of finely-divided charcoal and carbonate (*black flux*), from which the carbonate may be extracted by water. The carbonaceous residue left upon igniting alkaline earthy tartrates contains an insoluble carbonate, and effervesces when treated with dilute hydrochloric acid. Tartrates of the heavy metals also undergo decomposition, accompanied by the characteristic odour of burnt sugar, and leave much carbon mixed with metallic oxide or metal.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF TARTARIC ACID, and for some reactions A SOLUTION OF A NORMAL SALT (*Rochelle salt*, or potassic sodic tartrate).

The alkaline tartrates are soluble in water, the acid salts less so than the neutral tartrates. *The normal tartrates of the alkaline earthy bases, of the earths and heavy metals, are difficultly soluble in water*, but dissolve readily in dilute tartaric acid. Alkalies fail to precipitate double tartrates, readily soluble in water, containing an alkaline and metallic base. Hence *the presence of tartaric acid serves to prevent the precipitation* of $\mathbf{Fe}_2O_3$, $\mathbf{Cr}_2O_3$, $\mathbf{Al}_2O_3$, $\mathbf{Zn}O$, $\mathbf{Ni}O$, $\mathbf{Co}O$, $\mathbf{Mn}O$, $\mathbf{Cu}O$, $\mathbf{Pb}O$, $\mathbf{Bi}_2O_3$, $\mathbf{Pt}O_2$ or $\mathbf{Cd}O$; whilst some other substance, *e.g.*, $\mathbf{P}OHo_3$, if present, may be precipitated from an alkaline solution.

KCl (or some other potassium salt, especially the acetate) produces in a solution of free tartaric acid a *heavy white crystalline* precipitate of **hydric potassic tartrate**, $\overline{T}HoKo$, readily soluble in mineral acids and in alkalies and alkaline carbonates, insoluble in acetic acid. The precipitation is accelerated by agitation. Alkalies dissolve the precipitate, forming a normal tartrate, soluble in water, from which acetic acid reprecipitates the hydric potassic tartrate.

$\mathbf{Ca}Ho_2$ added in excess precipitates free tartaric acid as a *white* **calcic tartrate**, $\overline{T}Cao''$.

$\mathbf{Ca}Cl_2$ (but not $\mathbf{S}O_2Cao''$) precipitates from a solution of a normal tartrate, **white calcic tartrate** ($\overline{T}Cao''$, + 8 aq.), soluble in acids, even tartaric acid, in ammonic salts (AmCl), but not in ammonic hydrate. The precipitate is *soluble in cold potassic* or *sodic hydrate*, which is nearly free from carbonate, but is *reprecipitated on boiling* as a gelatinous mass, which *redissolves on cooling*.

$\mathbf{N}O_2Ago$ produces from a solution of a normal tartrate (*e.g.*, Rochelle salt) in the cold a *white curdy* precipitate of **argentic tartrate**, $\overline{T}Ago_2$. On filtering and dissolving some of the precipitate off the filter with a little dilute ammonic hydrate, and heating the solution in a clean test-tube or flask during ten to twenty minutes in water, heated to about 66° C., the glass becomes coated with a fine silver mirror. (CHARACTERISTIC REACTION FOR TARTARIC ACID.)

$\overline{Ac}_2Pbo''$ gives a *white crystalline* precipitate of **plumbic tartrate**, $\overline{T}Pbo''$, from solutions of tartaric acid or its soluble salts. The precipitate is soluble in nitric acid and in ammonic hydrate; the latter giving rise to the formation of plumbic ammonic tartrate, which cannot be precipitated by AmHo.

Tartaric acid and ammonia dissolve $\mathbf{S}O_2Pbo''$.

Concentrated $\mathbf{S}O_2Ho_2$ decomposes tartaric acid, or a tartrate, on heating, with evolution of $\mathbf{S}O_2$, $\mathbf{C}O_2$, and CO, and separation of carbon.

QUESTIONS AND EXERCISES.

1. Describe some sources of tartaric acid.
2. Describe the decomposition which tartaric acid and tartrates undergo upon ignition.
3. What is the composition of *black flux?*
4. Explain the solvent action of tartaric acid upon certain tartrates in the presence of alkalies.
5. How can tartaric acid be detected in the wet way?
6. Give graphic formulæ for Rochelle salt, argentic and plumbic tartrates.

CITRIC ACID, $\left\{\begin{array}{ll}\mathbf{C}HHo(COHo) & \\ \mathbf{C}H & (COHo)\\ \mathbf{C}H_2 & (COHo)\end{array}\right.$ + 2 aq., or briefly $\overline{Ci}Ho_3$.—*Tribasic* acid.—Obtained from orange or lemon-juice. Found also in many other fruits. It forms colourless prismatic crystals, which possess a pure and agreeable acid taste. They dissolve in cold and hot water, and in alcohol. The aqueous solution undergoes decomposition after a time. The *citrates* are very numerous, the acid forming, like phosphoric acid, three classes of salts by the replacement of one, two, or three atoms of hydroxyl by a corresponding amount of potassoxyl, etc.

REACTIONS IN THE DRY WAY.

On heating citric acid, it loses first its water of crystallisation, then fuses, and is decomposed with disengagement of pungent and irritating acid fumes, leaving a less abundant carbonaceous residue than tartaric acid. Alkaline and alkaline earthy citrates leave a carbonate upon ignition.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF $\overline{Ci}Ho_3$ IN WATER, OR A SOLUTION OF A NORMAL ALKALINE CITRATE.

Potassic salts give no precipitate.

$\mathbf{Ca}Ho_2$ gives no precipitate *in the cold* from a solution of citric acid, or of a neutral citrate; but *on heating*, a *white* precipitate of **calcic citrate**, $\overline{Ci}_2Cao''_3$ is obtained. (DISTINCTION BETWEEN TARTARIC AND CITRIC ACID.) When both citric and tartaric acid are present, the precipitate produced by $\mathbf{Ca}Ho_2$, or $\mathbf{Ca}Cl_2$ in the cold is filtered off, and the clear filtrate boiled, when a further precipitate indicates citric acid.

$\mathbf{Ca}Cl_2$ produces no precipitate *in the cold* from an aqueous solution of citric acid or a soluble citrate; on boiling, however, a white precipitate of calcic citrate is obtained, if the solution be neutral, or if it contain an excess of lime water or ammonic hydrate. This precipitate is *insoluble in sodic or potassic hydrate*, but soluble both in ammonic salts and in acids.

Argentic citrate, dissolved in ammonic hydrate, does not form a mirror upon heating. Citric acid, like tartaric acid, prevents the precipitation of certain oxides of Groups III and IV, by caustic alkalies, on account of the formation of soluble double citrates, containing a metallic and alkali base.

Concentrated sulphuric acid decomposes citric acid or citrates slowly. On cautiously applying heat, CO and CO_2 escape, at first without any blackening of the liquid, but on boiling for some time, SO_2 is evolved, and carbon separates.

QUESTIONS AND EXERCISES.

1. Whence is citric acid derived?
2. Describe the tests which distinguish citric from tartaric acid.
3. Give graphic formula for citric acid.
4. How would you detect oxalic, tartaric, and citric acids contained in a liquid?
5. Why does the presence of citric or tartaric acid prevent the precipitation of Al_2O_3 or Fe_2O_3 by AmHo?
6. How would you separate phosphoric acid by precipitation with a magnesic salt from a solution containing phosphates of Al^{iv}, Fe^{iv}, and Mn''?

PRACTICAL EXERCISES.

In order to enable the analyst to acquire a thorough mastery over the reactions for bases and acids, some 25 to 30 simple substances should be analyzed by the aid of the subjoined analytical tables, and the results recorded in the manner shown in the Appendix. The nature of these exercises will be sufficiently indicated by the following examples:—

1. Crystallized magnesic sulphate (Epsom salts).
2. Sodic sulphite.
3. Saltpetre.
4. Common sodic phosphate.
5. Potassic iodide.
6. Potassic oxalate.
7. Citric acid.
8. Calcic tartrate.
9. Sodic acetate.
10. Calcic phosphate.
11. Dried green vitriol.
12. Borax.

Preliminary to the analysis of more complex bodies, a number of double salts or mixtures of salts containing one or two bases and one, two or more acids should be next examined, such as:—

Ammonic ferrous sulphate.
Common ammonium or potassium alum.
Microcosmic salt.
Potassic sodic tartrate (Rochelle salt).
Dipotassic calcic ferrocyanide.
Potassic chlorate and potassic nitrate.
Sodic chloride and potassic chlorate.
Potassic oxalate and potassic carbonate.
Ammonic chloride and sodic nitrate.
Ammonic magnesic phosphate.
Potassic bromide and iodide, and sodic chloride.

Complex bodies should be examined systematically and the results carefully noted down in the analyst's laboratory book *immediately they are made*, and in the order indicated by the arrangement of the Analytical Tables. A careful preliminary examination in the dry way yields for the most part results which are decisive of the nature of the substance under examination. A few simple experiments are frequently sufficient to determine, in the case of simple salts, the nature of both base and acid, and in that of a compound substance, most bases and acids. Skill in blowpipe analysis is of paramount value in the analysis of well-defined minerals, as well as of complex mixtures. The student should, however, invariably control the results obtained by an examination of the solid substance in the dry way by a most searching analysis in the wet way.

The exercises should be progressive, and should at first consist of artificial mixtures of clearly-defined composition: and lastly, of complex bodies, such as minerals, alloys, colours, slags, refuse-matter from various manufacturing processes, etc.

The following mixtures or compound bodies may be taken as types of the 20 or 30 substances that should be examined in order to enable the student to acquire proficiency in qualitative analysis:—

1. $\mathbf{N}_2\mathrm{O}_4\mathrm{Pbo}''$,
   $\mathbf{H}\mathrm{gCl}_2$,
   AmCl,
   $\mathbf{C}\mathrm{OCao}''$.
2. $\mathbf{Ca}\mathrm{Cl}_2$,
   $\mathbf{Sr}\mathrm{Cl}_2$,
   $\mathbf{Ba}\mathrm{Cl}_2$.
3. $\mathbf{As}_2\mathrm{S}_3$,
   AmCl,
   $\mathbf{N}\mathrm{O}_2\mathrm{Ko}$.
4. Ammonium alum,
   Chrome alum,
   Galena.
5. Chrome iron ore.
6. Type metal.
7. Stourbridge fire-clay.
8. $\mathbf{Cr}\mathrm{O}_2\mathrm{Bao}''$,
   $\mathbf{Fe}_2\mathrm{O}_3$,
   $\mathbf{Ca}\mathrm{Cl}_2$,
   Sulphur.
9. $\mathbf{Ba}\mathrm{Cl}_2$,
   $\mathbf{P}\mathrm{OHoBao}''$,
   $\left\{\begin{array}{l}\mathbf{C}\mathrm{OKo},\\ \mathbf{C}\mathrm{OKo}.\end{array}\right.$
10. Ammonium alum,
    Chrome alum,
    $\mathbf{P}\mathrm{OHoNao}_2$,
    $\mathbf{Fe}_2\mathrm{O}_3$,
    $\mathbf{Si}\mathrm{O}_2$.
11. $\mathbf{C}\mathrm{OBao}''$,
    $\mathbf{P}_2\mathrm{O}_2\mathrm{Bao}''_3$,
    $\mathbf{S}\mathrm{O}_2\mathrm{Bao}''$,
    NaCl.
12. Ultramarine.
13. Guano.
14. Coprolite.
15. Material which has been used for purifying coal-gas.
16. Alkali waste.

TABLES

FOR THE

QUALITATIVE ANALYSIS

OF

SIMPLE AND COMPOUND SUBSTANCES, BOTH IN THE DRY AND WET WAY.

PRELIMINARY EXAMINATION OF SOLIDS IN THE DRY WAY.

The physical properties of a substance under examination, such as its crystalline structure, its odour, colour, metallic lustre, hardness, density, are capable of throwing, in many cases, much light upon its composition, and should be carefully noted before subjecting the substance to a qualitative analysis.

Experiment.	Observation.	Inference.
I. HEAT A SMALL PORTION OF THE SUBSTANCE, IN THE STATE OF POWDER, IN A DRY TEST-TUBE, OR A PIECE OF COMBUSTION TUBE, CLOSED AT ONE END.	THE SUBSTANCE DOES NOT CHANGE.	Absence of organic substances, of volatile inorganic matter, of substances decomposed on ignition, of hygroscopic moisture, of water of crystallisation, and of water of hydration.
	THE SUBSTANCE CHANGES.	
	(A.) *Without decomposition.*	
	1. *The substance changes colour*, yellow whilst hot, white on cooling	**ZnO**.
	From yellow to reddish brown whilst hot, yellow when cold, fusible at a red heat	**PbO**.
	From white to yellowish brown when hot, dirty light yellow on cooling	**Sn**O_2. [**Ti**O_2.]
	From white to orange and reddish brown, dull yellow on cooling, fusible at an intense heat	**Bi**$_2O_3$.
	Dark red whilst hot, reddish brown on cooling	**Fe**$_2O_3$.
	2. *The substance fuses* and re-solidifies when the flame is removed	Mostly salts of the alkalies, and some salts of the alkaline earths (nitrates, chlorides, etc.).
	3. *The substance sublimes.*	Several compounds of ammonium, mercury, and arsenic, also sulphur and

		iodine (plumbic chloride sublimes difficultly). Volatile organic acids, *e.g.*, oxalic, benzoic, and succinic acids.
	The substance melts at a very gentle heat, heavy fumes appear in the tube, and the sublimate is white and crystalline	$\mathbf{Hg}Cl_2$.
	It sublimes without previous fusion, is yellow when hot, white when cold	$\mathbf{Hg}_2Cl_2$.
	The sublimate is black, and turns red on rubbing	$\mathbf{Hg}S$.
	The sublimate is yellow	$\mathbf{Hg}I_2, \mathbf{As}_2S_3$.
	It consists of reddish brown drops, yellow when cold	Free sulphur.
	The sublimate consists of white octohedral crystals	$\mathbf{As}_2O_3$.
	The substance fuses into a yellow mass, and at a red heat sublimes entirely, forming crystalline needles	$\mathbf{Sb}_2O_3$.
	Violet vapour, feathery bluish-black crystals	Iodine.
	Odour of frankincense	Benzoic acid.
	Fumes which cause violent coughing	Succinic acid.
	Heavy white fumes, and white crystalline sublimate	Oxalic acid.
Confirm by heating a little of the dry substance with dry $\mathbf{C}ONao_3$, or black flux, in a bulb-tube.	Metallic mirror and globules of a metal	Mercury compounds.
	Black shining mirror, no metallic globules	Arsenical compounds.
	$\mathbf{N}H_3$ is given off	Ammonium compounds.
	$\mathbf{C}O_2$ is evolved	A free acid, *e.g.*, $\mathbf{As}_2O_3$, $\mathbf{As}_2O_5$, oxalic, benzoic, and succinic acids.
Test also specially for ammonium compounds by mixing a little of the substance in a mortar with soda-lime, and moistening with a few drops of water.	Odour of $\mathbf{N}H_3$	Ammonium compounds ($\mathbf{C}OAmo_3$, $\mathbf{P}OAmo_3$, $\mathbf{B}Amo_3$, are decomposed, and give off $\mathbf{N}H_3$ when heated by themselves).

PRELIMINARY EXAMINATION OF SOLIDS IN THE DRY WAY.—*continued.*

Experiment.	Observation.	Inference.
Confirm oxalic acid by heating in a test-tube with a little concentrated $\mathbf{S}O_2Ho_2$.	CO and $\mathbf{C}O_2$ are evolved	$\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}OHo\end{array}\right.$
	(B.) ***With partial or total decomposition.***	
	1. ***The substance fuses, and gives off water of hydration*** (sometimes without fusion), or water of *crystallisation*, becoming liquid at a low heat, *i.e.*, it fuses in its water of crystallisation; it then solidifies and fuses again when heated more strongly (igneous fusion), and swells up, or intumesces, considerably	**Metallic hydrates.** Salts containing water of crystallisation, *e.g.*, phosphates, borates, alums, &c.
Confirm by examining the condensed water with litmus-paper.	Alkaline reaction	Ammonium compounds.
	Acid reaction	Free volatile acids, such as $\mathbf{N}O_2Ho$, HCl, $\mathbf{S}O_2Ho_2$, $\mathbf{S}OHo_2$, &c., or acid salts.
	2. ***The substance gives off a gas or condensable vapour, with or without change of colour***	
Confirm by introducing a glowing splinter of wood into the test-tube.	Oxygen is given off, causing a glimmering splinter of wood to burst into flame, and to burn most brilliantly	Metallic peroxides, chlorates, perchlorates, nitrates, bromates, iodates.
	Oxygen mixed with other gases, *e.g.*, $\mathbf{S}O_2$, N, $\mathbf{N}_2O_4$, Cl, Br, I, is given off	From the decomposition of certain sulphates, of nitrates, nitrites, chlorates, hypochlorites, bromates, iodates.
Confirm by passing the gas through an acidulated solution of an alkaline chromate.	$\mathbf{S}O_2$ is given off, recognized by its suffocating odour, and its acid reaction with test-paper	Acid sulphites; also from the decomposition of sulphates, with or without evolution of oxygen, of earthy sulphites or hyposulphites; from the action of organic matter

Heat also a little of the powdered substance in a piece of combustion tubing, open at both ends.		upon sulphates, and from the oxidation of metallic sulphides and sulphocyanates.
Pass the gas through water and collect oxygen separately.	$\mathbf{N}_2O_4$ and oxygen or reddish-brown fumes come off; the oxygen gas supports combustion	Nitrates of heavy metals, *e.g.*, of Pb, Bi.
Confirm by passing gas through lime- or baryta-water.	$\mathbf{C}O_2$ is given off, which is a non-supporter of combustion. The gas precipitates lime- or baryta-water	From the decomposition of carbonates; (alkaline carbonates excepted), also from the decomposition of oxalates and cyanates.
Absorb the $\mathbf{C}O_2$ by passing the gas through baryta-water before collecting and igniting the CO gas.	CO is evolved, burning with a blue flame ..	From oxalates and formates.
The same applies to cyanogen gas, when mixed with $\mathbf{C}O_2$.	CN is given off, having a peculiar odour, and burning with peach-blossom coloured flame	From cyanides of Ag, Hg, Cu, Zn, also from cyanates and sulphocyanates.
	Nitrogen, a non-supporter of combustion ..	$\mathbf{N}$OAmo, or some fixed nitrite in the presence of ammonic salts (AmCl, etc.)
	$\mathbf{O}N_2$, supporting combustion	$\mathbf{N}O_2$Amo, or some fixed nitrate in the presence of Ammonic salts.
	$\mathbf{S}H_2$ gas, recognized by its odour and action on lead paper	Hydrated sulphides, moist sulphites and hyposulphites.
	$\mathbf{N}H_3$, possessing a characteristic pungent odour and alkaline reaction to test-paper	From ammonic salts, such as $\mathbf{C}$OAmo$_2$, and others containing fixed acids (phosphates, borates); from cyanates in the presence of water, and from the decomposition of organic substances containing nitrogen, accompanied by carbonization and evolution of offensive empyreumatic oils.
	$\mathbf{C}S_2$ is sometimes given off	From the decomposition of sulphocyanates.
Confirm by passing the gas through a solution of potassic iodide, and starch paste.	Cl is given off, recognized by its pungent odour. The gas bleaches vegetable colours and liberates iodine from KI.	Several chlorides, such as the chlorides of the noble metals Pt, Au; also from certain chlorates and hypochlorites.

PRELIMINARY EXAMINATION OF SOLIDS IN THE DRY WAY.—*continued.*

Experiment.	Observation.	Inference.
	Br and I are given off, recognized by the odour of their vapour or sublimate, and their action on starch paste	Several bromides and iodides when heated by themselves with exclusion of air, or in the presence of atmospheric air; in the latter case with formation of oxides; also some bromates and iodates.
	Sulphur vapour, which condenses in the upper part of the tube in yellow drops, and burns with blue flame ..	From the decomposition of metallic persulphides, *e.g.*, PtS_2, Au_2S_3, Sb_2S_5, SnS_2, FeS_2, which leave either a lower sulphide or the metal.
	3. The *substance becomes carbonized and evolves empyreumatic and other gaseous products of decomposition*	From the decomposition of organic substances.
	Acetone is given off	From the decomposition of acetates.
Confirm by treating the residue with dilute hydrochloric acid.	A carbonate is left which effervesces with dilute acids, whilst the original substance does not effervesce	Organic acids, combined with alkaline, or alkaline earthy bases.
	The carbonate is soluble in water, and the solution has an alkaline reaction	Organic compounds of the fixed alkali metals.
	The carbonate is insoluble in water	Organic acids, combined with alkaline earthy metals.
II. HEAT A LITTLE OF THE SUBSTANCE UNDER EXAMINATION ON CHARCOAL BEFORE THE BLOWPIPE FLAME. (Comp. chapter on The Blowpipe and its Use.)	1. *The substance decrepitates.*	NaCl, &c., &c.
	2. *The substance deflagrates.*	Nitrates, chlorates, &c.
	3. *The substance fuses readily and sinks into the charcoal, or forms a liquid bead*	Salts of alkalies and some salts of alkaline earths.
	4. *An infusible residue is left.*	

	(a.) *The residue is white* and highly luminous	$\mathbf{Ba}O$, $\mathbf{Sr}O$, $\mathbf{Ca}O$, $\mathbf{Mg}O$, $\mathbf{Al}_2O_3$, $\mathbf{Zn}O$, also $\mathbf{Si}O_2$.
Confirm by treating the white infusible residue when cold with a few drops of $\mathbf{N}_2O_4Coo''$, and ignite again strongly.	Alkaline to test-paper	$\mathbf{Ba}O$, $\mathbf{Sr}O$, $\mathbf{Ca}O$, $\mathbf{Mg}O$.
	A fine blue mass is left	$\mathbf{Al}_2O_3$, alkaline earthy phosphates, $\mathbf{Si}O_2$, and many silicates.
	A flesh-coloured (or pink) mass is left	$\mathbf{Mg}O$.
	„ green „ „	$\mathbf{Zn}O$.
	(b.) *The residue is coloured*	$\mathbf{Cu}O$, $\mathbf{Co}O$, $\mathbf{Ni}O$, $\mathbf{Mn}O$, $\mathbf{Fe}_2O_3$ $\mathbf{Cr}_2O_3$.
Confirm by heating a small quantity of the residue in a clear borax bead on a platinum-wire, in the inner and outer blowpipe flame.	Oxidizing flame: green bead whilst hot, blue when cold. Reducing flame: red bead when cold	$\mathbf{Cu}O$.
	Blue bead both in the oxidizing and reducing flame	$\mathbf{Co}O$.
	Hyacinth-red to violet-brown bead when hot, yellowish to sherry-red when cold	$\mathbf{Ni}O$.
Confirm the presence of Mn also by fusion with nitre and $\mathbf{C}ONao_2$ on platinum-foil.	Amethyst-red bead in oxidizing flame. Colourless bead in reducing flame (not quite clear)	$\mathbf{Mn}O$.
	Brownish-red bead when hot, light yellow or colourless when cold in the oxidizing flame; an olive-green to bottle-green bead in the reducing flame	$\mathbf{Fe}_2O_3$ or $\mathbf{Fe}O$.
Confirm the presence of Cr by fusion with nitre and fusion-mixture on platinum-foil.	Green in oxidizing flame, ditto in reducing flame	$\mathbf{Cr}_2O_3$.
III. HEAT IN THE INNER BLOWPIPE FLAME.	1. *The substance colours the outer flame.*	
Confirm by heating a little of the substances on a clean platinum wire. (The chlorides of the different metals answer best. Borates should be decomposed with $\mathbf{S}O_2Ho_2$.)	Golden-yellow	Na compounds.
	Violet	K „
	Yellowish-green	Ba „
	Crimson	Sr „
	Reddish	Ca „
	Green	Cu, $\mathbf{B}_2O_3$.

PRELIMINARY EXAMINATION OF SOLIDS IN THE DRY WAY.—*continued.*

Experiment.	Observation.	Inference.
	Blue	As, Sb, Pb, $\mathbf{Cu}Cl_2$.
	2. *The substance is reduced to the metallic state; the metal is volatile, and on passing through the outer flame yields an incrustation.*	
	A white incrustation and characteristic garlic odour	Compounds of arsenic.
	Incrustation yellow when hot, white when cold	Zn.
	Incrustation reddish-brown (readily volatilized)	Cd.
	3. *The substance is reduced to the metallic state*	Au, Ag, Cu, Pb, Sn, Sb, Bi (also Co, Ni, Fe).
Confirm by mixing a little of the substance with $\mathbf{C}ONao_2$ and KCy, and heating on charcoal in the inner blowpipe flame.	(A.) *Without incrustation.*	
	Brilliant white metal	Ag.
	Yellow metal	Au.
	Red scales or globules of a red metal.. ..	Cu.
	Metallic powders which cannot be fused into globules, but are magnetic	Fe, Co, Ni.
	(B.) *With incrustation..*	Sn, Pb, Bi, Sb.
	Metal malleable; slight incrustation, which is yellow when hot, white when cold	Sn.
	Metal brittle; incrustation dark orange when hot, lemon-yellow when cold	Bi.
	Metal malleable; incrustation lemon-yellow whilst hot, yellow when cold	Pb.

	Metal brittle; gives off white fumes when withdrawn from the flame, and becomes surrounded with a net work of brilliant acicular crystals of Sb_2O_3; incrustation white and close to the substance	Antimony compounds.
Heat a little of the substance mixed with dry $CONao_2$ (free from sulphate) in the reducing flame; place the fused mass on a bright silver coin and moisten it with water.	An alkaline sulphide is left; the silver is stained black, and the fused mass evolves SH_2 when heated with dilute HCl	Presence of sulphur, either in the form of a sulphide, or of a salt of an oxygen acid of sulphur.

Note 1.—Many of the changes observed on heating a substance by itself in a tube closed at one end occur again, when the substance is heated on charcoal, but may be neglected, as they are so much more readily studied by heating the substance in a tube.

Note 2.—A substance under examination may consist of several bodies, and the reactions which it gives may frequently obscure each other. Analytical tables, moreover, cannot possibly provide an explanation for every change that may be produced during the preliminary examination of a mixture of several substances. The analyst should, therefore, record faithfully every observation which he makes, though he may not be able at the time to draw an inference from it, and should endeavour to elicit by further experiments what substances are present in the mixture which he is called upon to examine in the dry way.

Absolute proof can, in many cases, only be obtained by an examination of a substance in the wet way.

Examination of a Substance in the Wet Way.

1st. *The substance under examination is a liquid.*—Examine it by means of well-prepared test-papers. The liquid is *neutral*. This excludes a large number of substances, since the greater proportion of normal salts of the metals possess an acid reaction. (Compare chapters XX and XXI, Part I.) The liquid shows an *acid* reaction. This may arise from a free acid, or from the presence of a normal salt having an acid reaction, or, lastly, from an acid salt. Or the solution possesses an *alkaline* reaction, owing to the presence of a salt of alkaline reaction, of free alkalies or alkaline earths, and of cyanides or sulphides of the alkalies or alkaline earthy metals.

Evaporate a portion of the liquid to dryness on a watch-glass or platinum foil. It leaves no residue, and may consist of pure water only; or it leaves a residue; a larger portion of the liquid should then be evaporated to dryness in a porcelain dish and subjected to a preliminary examination in the dry way.

2nd. *The substance under examination consists of a solid body.*—If it occurs in large pieces, or in the form of a coarse powder, it should first be reduced by mechanical means to as fine a powder as possible. Natural silicates and other compounds which are decomposed with difficulty by acids, are finely powdered in an agate mortar and then *levigated*, *i.e.*, stirred up repeatedly with water; the coarser particles of the powdered substance fall rapidly to the bottom, and the water holding the finer particles in suspension can be poured off. The coarser particles must then be ground again, and made to pass through a fresh process of levigation, till the *whole* of the substance is obtained in an equally fine state of division. By allowing the water to stand for some time, the whole of the suspended particles fall to the bottom of the vessel, and can be separated by decantation and filtration.

Ascertain whether the solid substance is *wholly* or *partly* soluble in water. This is done by boiling about a gramme of it in distilled water, allowing the undissolved portion to subside before decanting the supernatant liquid, and treating the undissolved portion again with boiling water as long as anything is dissolved. A drop of the solution, when evaporated on a watch-glass or on platinum foil, should leave a visible spot.

The *aqueous extract* is set aside until the residue has in like manner been treated with acids. It should be tested with litmus-paper.

The *residue insoluble in water* is next treated with dilute hydrochloric acid, and heated for some time to boiling. The undissolved portion is allowed to subside and the clear fluid decanted. This operation should be repeated several times, both with dilute and concentrated hydrochloric acid. Boiling with HCl generally dissolves out whatever is soluble, and NO_5HO has rarely to be resorted to. If an insoluble residue be left, treat with small quantities of aqua regia. Observe carefully what changes take place when the substance is treated with acids, especially whether any and what gases are disengaged.

The *residue insoluble in water and acids* should be carefully washed with distilled water, filtered, dried, and then mixed with three to four times its weight of dry $\mathbf{C}ONao_2$ and $\mathbf{C}OKo_2$ (fusion-mixture) and fused. The fusion is best performed in a platinum crucible, provided the insoluble residue does not contain any metals capable of forming alloys with platinum. This can be readily ascertained by an examination of the residue in the dry way.

It should be borne in mind that only BARIC, STRONTIC, CALCIC, AND PLUMBIC SULPHATES; PLUMBIC AND ARGENTIC CHLORIDES; $\mathbf{Si}O_2$, MANY SILICATES; NATIVE OR IGNITED $\mathbf{Al}_2O_3$ AND ALUMINATES; IGNITED $\mathbf{Cr}_2O_3$ and $\mathbf{Fe}_2O_3$; CHROME IRON ORE; $\mathbf{Sn}O_2$ (IGNITED OR AS TINSTONE); IGNITED $\mathbf{Sb}_2O_4$ (A FEW METAPHOSPHATES AND ARSENATES); $\mathbf{Ca}F_2$, AND A FEW OTHER NATIVE FLUORIDES; SULPHUR AND CARBON, are likely to be present in the residue.

Ag_4FeCy_6 and $Ag_6Fe_2Cy_{12}$, AgBr, AgI, and AgCy are decomposed into AgCl by boiling with aqua regia.

Solutions 1 and 2 may be examined separately, or they may be mixed and examined together. A separate analysis of the aqueous and acid extracts becomes necessary only when it is intended to show *how* the acids and bases are combined in a compound body.

The examination of a residue requiring fusion with alkaline carbonates is invariably conducted separately. The fused mass is boiled with water and filtered; the powder, insoluble in water, containing the base in the form of a carbonate (oxide or metal) is dissolved in HCl or $\mathbf{N}O_2Ho$. The aqueous extract is examined for acids, and the acid extract for bases.

Alloys are dissolved in dilute or concentrated HCl, sometimes with the aid of platinum foil, or with the addition of a few crystals of potassic chlorate and their solutions examined as usual.

Cyanogen compounds are best destroyed by fusion in a porcelain crucible with 3 or 4 times their weight of a mixture of 3 parts of $\mathbf{S}O_2Amo_2$ and 1 part of $\mathbf{N}O_2Amo$. The metals can then be detected in the residue in the usual manner.

Remark.—In order to economize time, the solution of a substance should be prepared at the same time as the examination in the dry way is conducted, and whilst the separation into groups is effected by means of the several group-reagents. The precipitates can then be well washed. Again, the time occupied in the evaporation of the filtrate from Group II, and in separating Fe^{iv}, Cr^{iv}, and Al^{iv} by means of $\mathbf{C}OBao''$ in Group III, may be employed in the examination of the precipitate produced by HCl or $\mathbf{S}H_2$, as well as in detecting the acids in the dry and wet way.

GENERAL TABLE FOR THE

To the greater portion of the original solution add HCl, as

The PRECIPITATE may contain— $PbCl_2$, white $AgCl$, „ Hg_2Cl_2 „ (Note 2.) Examine by Table I.	The FILTRATE (Note 3) is largely
	The PRECIPITATE may contain— HgS, black PbS, „ Bi_2S_3, „ CuS, „ CdS, yellow Insoluble in NaHo or SAm_2. SnS, brown SnS_2, yellow Sb_2S_3, orange Sb_2S_5, „ As_2S_3, yellow Au_2S_3, black PtS_2, „ Soluble in NaHo or SAm_2. Examine by Table II.

EXAMINATION OF BASES.

long as a precipitate is produced, and heat gently. (Note 1.)

diluted with water (Note 4), saturated with $\mathbf{S}H_2$, and gently heated (Note 5 and 6).

Evaporate the FILTRATE till free from $\mathbf{S}H_2$, then add a few drops of concentrated $\mathbf{N}O_2Ho$, and evaporate to complete dryness. If oxalates or organic matter (Note 7) be suspected (indicated by the blackening of the residue), heat to redness in a porcelain dish, but not otherwise. Treat the residue with a little concentrated HCl, add water and heat, when it dissolves either wholly or leaves a white residue of $\mathbf{Si}O_2$ (Note 8). Test a small portion of the HCl solution with ammonic molybdate.

(A.) *No precipitate is obtained*, $\mathbf{P}OHo_3$ **is absent.**—Add AmCl, AmHo, and $\mathbf{S}Am_2$ to the remaining portion of the solution, heat to boiling, and filter quickly; wash well with hot water containing a little $\mathbf{S}Am_2$.

(B.) *A precipitate is obtained*, $\mathbf{P}OHo_3$ **is present.**—Add AmCl and AmHo in slight excess to the remaining portion of the solution, heat gently and filter quickly; wash well with hot water. To the filtrate add $\mathbf{S}Am_2$ to slight excess, heat to boiling and filter. Wash with hot water containing a few drops of $\mathbf{S}Am_2$, and examine filtrates under Group IV. Transfer the two precipitates to a porcelain dish, and digest with a little $\mathbf{S}Am_2$ (Note 9). Filter off and wash well. Neglect filtrate (Note 10).

(A.)	(B.)	To the FILTRATE from III A or III B add AmHo and $\mathbf{C}OAmo_2$, heat gently (Note 12) and filter.	
The PRECIPITATE may contain—	The PRECIPITATE may contain—	The PRECIPITATE may contain—	SOLUTION may contain—
$\mathbf{Al}_2Ho_6$, yellowish-white, gelatinous. $\mathbf{Cr}_2Ho_6$, bluish-green. $\mathbf{Fe}S$, black. $\mathbf{Zn}S$, white. $\mathbf{Mn}S$, flesh-coloured. $\mathbf{Ni}S$, black. $\mathbf{Co}S$, „	$\mathbf{Al}_2Ho_6$, yellowish-white gelatinous. $\mathbf{Cr}_2Ho_6$, bluish-green. $\mathbf{Fe}S$, black. $\mathbf{Zn}S$, white. $\mathbf{Mn}S$, flesh-coloured. $\mathbf{Ni}S$, black. $\mathbf{Co}S$, „ Together with the phosphates of (Cr) and Al, as well as of the alkaline earthy metals. (Note 11.)	$\mathbf{C}OBao''$, white. $\mathbf{C}OSro''$, „ $\mathbf{C}OCao''$, „	$\mathbf{Mg}O$. $\mathbf{O}K_2$. $\mathbf{O}Na_2$.
Examine by Table III A.	Examine by Table III B.	Examine by Table IV.	Examine by Table V.

NOTES TO GENERAL TABLE.

1. In case the original substance had to be dissolved in hydrochloric acid $\mathbf{S}H_2$ may be passed at once.

2. In a saturated solution of a baric salt, HCl produces a white precipitate, soluble in hot water. From an alkaline solution HCl may precipitate $\mathbf{Si}Ho_4$ (gelatinous), $\mathbf{B}Ho_3$, $\overline{Bz}Ho$ [and uric acid} crystalline, also $\mathbf{Sb}_2O_5$ (amorphous). Metallic oxides, such as $\mathbf{Al}_2O_3$ and metallic sulphides, such as $\mathbf{As}_2S_3$, $\mathbf{Sb}_2S_3$, $\mathbf{Sb}_2S_5$, $\mathbf{Sn}S$, and $\mathbf{Sn}S_2$, which dissolve in NaHo or $\mathbf{S}Am_2$, may likewise be precipitated on the addition of HCl, and are best examined separately.

3. If arsenic has been detected in the preliminary examination, this filtrate, which may contain pentad arsenic, should be boiled with a solution of $\mathbf{S}OHo_2$, or $\mathbf{S}OHoAmo$, then evaporated considerably to expel the $\mathbf{S}O_2$. Ba, Sr, and Pb, when present, may be precipitated either partly or wholly, as sulphates. The precipitate is best examined separately.

4. Certain oxychlorides, *e.g.*, of Bi, Sb, or Sn, may be precipitated on the first addition of dilute HCl or water, but are readily redissolved on the addition of more acid, and on gently heating; or the precipitate may be disregarded, since $\mathbf{S}H_2$ readily converts the finely divided oxychlorides into the corresponding metallic sulphides.

5. $\mathbf{S}H_2$ often produces merely a precipitation of sulphur, owing to the presence of oxidizing agents, such as Cl, Br, I, ($\mathbf{S}OHo_2$, $\mathbf{N}OHo$), $\mathbf{N}O_2Ho$, ClHo, $\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}Ho\end{matrix}\right.$, $\left\{\begin{matrix}\mathbf{O}I\\ \mathbf{O}Ho\end{matrix}\right.$, $\left\{\begin{matrix}\mathbf{O}Br\\ \mathbf{O}Ho\end{matrix}\right.$, and $\mathbf{Cr}O_2Ho_2$, or of ferric salts. This precipitate is easily distinguished by its being white and remaining suspended in the solution. It may be neglected altogether. A brick red precipitate of $\left\{\begin{matrix}\mathbf{Pb}Cl\\ S\\ \mathbf{Pb}Cl\end{matrix}\right.$ sometimes comes down from strongly acid (HCl) solutions, if the solution has not been sufficiently diluted with water.

6. $\mathbf{S}H_2$ should be passed once more through the filtrate, to make sure of the complete precipitation of all the metals of Group II.

7. Organic acids, *e.g.*, $\overline{T}Ho_2$, $\overline{Ci}Ho_3$, also sugar, etc., prevent the precipitation of $\mathbf{Al}_2Ho_6$, etc., in Group III. (Comp. p. 296.)

8. It is possible that this $\mathbf{Si}O_2$ may be mixed with other substances, *e.g.*, $\mathbf{Al}_2O_3$, $\mathbf{Cr}_2O_3$, $\mathbf{Fe}_2O_3$ (rendered insoluble by strong ignition), $\mathbf{S}O_2Bao''$, $\mathbf{S}O_2Sro''$, in which case it is necessary to examine it separately.

9. If the $\mathbf{S}Am_2$ were added simultaneously with the AmCl and AmHo, phosphates of Fe, Mn, Zn, Ni, and Co would be decomposed into sulphides, with formation of $\mathbf{P}OAmo_3$, which might produce a precipitate of a phosphate of the alkaline earthy bases, by acting upon salts of these bases other than phosphates, or act as a solvent for other phosphates in the presence of AmHo. (Comp. p. 179.)

10. This filtrate may contain $\mathbf{P}OHo_3$, a proof that a phosphate of the metals Fe, Zn, Mn, Ni, or Co was present in the original HCl solution, or, *vice versâ*, that all these metals (or one or several of them) may be present. (Comp. p. 179.)

11. Small quantities of borates and fluorides of the alkaline earthy metals may likewise be precipitated, together with the alkaline earthy phosphates, but need not be examined further, since their bases will be detected in Group IV, and their acids on examining in the usual way for acids.

12. The solution must not be boiled, since the AmCl, by double decomposition, dissolves the alkaline earthy carbonates, forming chlorides and ammonic carbonate, which volatilizes with the aqueous vapour.

TABLE I.—SEPARATION OF THE METALS OF GROUP I.

The precipitate may contain $\mathbf{Pb}\mathrm{Cl_2}$, AgCl, $\mathbf{Hg}_2\mathrm{Cl_2}$, also $\mathbf{B}\mathrm{Ho_3}$, $\bar{\mathrm{B}}\mathrm{zHo}$ (uric acid) (Note 1). Wash the precipitate on the filter with hot water till it is quite free from $\mathbf{Pb}\mathrm{Cl_2}$.		
The SOLUTION may contain $\mathbf{Pb}\mathrm{Cl_2}$ On cooling white acicular crystals fall out. Confirm by $\mathbf{Cr}\mathrm{O_2Ko_2}$, or $\mathbf{S}\mathrm{O_2Ho_2}$. **Presence of Pb.**	The white RESIDUE may consist of AgCl, $\mathbf{Hg}_2\mathrm{Cl_2}$; heat gently with excess of dilute AmHo.	
	The SOLUTION may contain AgCl; acidulate with dilute $\mathbf{N}\mathrm{O_2Ho}$. A white curdy precipitate of AgCl is obtained. **Presence of Ag.**	The RESIDUE is black, consisting of $\mathbf{N}\mathrm{H_2{}'Hg'_2Cl}$. Confirm by drying residue and heating with dry $\mathbf{C}\mathrm{ONao_2}$ in a bulb-tube. A metallic mirror and globules indicate— **Presence of Hg** (as mercurosum).

Note 1.—Unless HCl be added in excess, and the solution gently heated, certain oxychlorides of Bi and Sb, as well as Sn (likewise $\mathbf{Si}\mathrm{Ho_4}$, and a few other substances) may become precipitated in this group.

TABLE II.—SEPARATION OF

The precipitate may contain HgS, PbS, Bi_2S_3, CuS, CdS, SnS, SnS_2, Sb_2S_3, Sb_2S_5, As_2S_3,
Comp. p. 219.) Wash the precipitate until free from

<table>
<tr><td colspan="5">Residue.—Wash well; boil in a little concentrated NO_2Ho until all action ceases. Dilute with water; add dilute SO_2Ho_2, as long as a precipitate is produced; allow to cool and add an equal bulk of alcohol (methylated); filter.</td></tr>
<tr><td colspan="2">Residue.—Boil in ammonic acetate: SO_2Pbo'' dissolves; allow to cool and filter.</td><td colspan="3">Solution.—Boil off the alcohol, add excess of AmHo; boil and filter.</td></tr>
<tr><td rowspan="2">Residue consists of HgS and S, or of S only.
Confirm by reducing the dried HgS in a bulb-tube with dry $CONao_2$.
Metallic mirror and globules.
Presence of Hg. (as mercuricum.)</td><td rowspan="2">Solution.—Add CrO_2Ko_2, yellow precipitate of CrO_2Pbo''.
Presence of Pb.</td><td rowspan="2">The precipitate consists of $BiHo_3$. Dissolve in a few drops of dilute HCl; evaporate nearly to dryness and add water. Milkiness from $BiOCl$.
Presence of Bi.</td><td colspan="2">Solution.—Acidulate with HCl and pass SH_2; filter off and wash the precipitate with weak SH_2 water. Boil with dilute SO_2Ho_2 and filter.</td></tr>
<tr><td>Residue. — Dissolve in NO_2Ho; add slight excess of AmHo, then $\left\{\begin{matrix} CH_3 \\ COHo, \end{matrix}\right.$ and K_4FeCy_6. Brown precipitate of Cu_2FeCy_6.
Presence of Cu.</td><td>Solution.—Add AmHo and pass SH_2. Yellow precipitate of CdS.
Presence of Cd.</td></tr>
</table>

Note 1.—CuS is somewhat soluble in SAm_2 and HgS in SNa_2. It is therefore advisable to
If both CuS and HgS are present dissolve in

THE METALS OF GROUP II.

<table>
<tr><td colspan="3">(Au and Pt must be tested for specially in a separate portion of the filtrate from Group I. HCl; boil with NaHo, or $\mathbf{S}Am_2$ and filter (Note 1).</td></tr>
<tr><td colspan="3">Solution may contain As, Sb, Sn (Au and Pt) as sulpho-salts. Acidulate with dilute hydrochloric acid, $\mathbf{As_2}S_3$, $\mathbf{Sb_2}S_5$, and $\mathbf{Sn}S_2$ are reprecipitated. Filter and wash; digest with $\mathbf{C}OHoAmo$ and filter.</td></tr>
<tr><td colspan="2">Residue consists of $\mathbf{Sb_2}S_5$ and $\mathbf{Sn}S_2$ Dissolve in boiling HCl. Introduce into a Marsh's apparatus in which hydrogen is generated by means of pure Zn and HCl.</td><td rowspan="2">Solution contains $\mathbf{As_2}S_3$. Reprecipitate by adding HCl. Confirm the presence of As by reducing with KCy and $\mathbf{C}ONao_2$ in a bulb-tube.
Metallic mirror and garlic odour.

Presence of As.</td></tr>
<tr><td>$\mathbf{Sb}H_3$ comes off. Collect as metallic Sb on porcelain or glass and identify the deposited metal by means of ClNao or dry HCl gas.

Presence of Sb.</td><td>The Residue in the generating flask consists of Zn and Sn.
Detach the precipitated Sn from the strips of zinc; wash and dissolve in a little concentrated HCl by the aid of platinum-foil. Dilute with water, and add $\mathbf{Hg}Cl_2$. A white precipitate of $\mathbf{Hg_2}Cl_2$ or of grey metallic Hg is obtained.

Presence of Sn.</td></tr>
</table>

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dissolve the precipitate in the absence of $\mathbf{Cu}S$ with $\mathbf{S}Am_2$, and in the absence of $\mathbf{Hg}S$ with $\mathbf{S}Na_2$. $\mathbf{S}Am_2$, when a little $\mathbf{Cu}S$ will be found in the solution.

TABLE III A.—SEPARATION OF THE

A. $POHo_3$ is absent.—Dissolve the precipitate from Group IIIA. in a little dilute HCl, with the is perceptible. Filter off sulphur if necessary. Neutralize solution with $CONao_2$; add possible. Pour off the clear liquid; throw the precipitate on a filter and wash with hot water.

<table>
<tr><td colspan="4">SOLUTION.—Remove $BaCl_2$ by adding a few drops of dilute SO_2Ho_2; boil, allow to subside, and filter off SO_2Bao''. Nearly neutralize the filtrate with $CONao_2$, and add pure NaHo, till the solution becomes alkaline; boil and filter.</td></tr>
<tr><td rowspan="3">The SOLUTION may contain zinc as $ZnNao_2$. Add SH_2. White precipitate of ZnS.
Presence of Zn.</td><td colspan="3">The PRECIPITATE may contain $MnHo_2$, $CoHo_2$ and $NiHo_2$. Wash, dissolve in a little dilute HCl; nearly neutralize with AmHo; add excess of $\left\{\begin{array}{l}CH_3\\COAmo\end{array}\right.$; pass a rapid current of SH_2 for several minutes through the solution and filter.</td></tr>
<tr><td rowspan="2">The SOLUTION contains the manganese as acetate.
Add AmCl, AmHo and SAm_2.
Flesh-coloured precipitate of MnS.
Presence of Mn.</td><td colspan="2">RESIDUE.—Dissolve in HCl and $\left\{\begin{array}{l}OCl\\OKo\end{array}\right.$; nearly neutralize with $CONao_2$; add a weak solution of KCy, so as just to redissolve the precipitate first produced. Boil briskly for some time, allow to cool (filter off any slight precipitate), and add a strong solution of ClNao; allow to stand for some time in a warm place, as long as a black precipitate forms, and filter.</td></tr>
<tr><td>PRECIP. — Ni_2Ho_6. Confirm by heating a small portion of it on a borax-bead before the blowpipe flame.
A yellowish to sherry-red bead.
Presence of Ni.</td><td>The SOLUTION contains the cobalt as $K_6Co_2Cy_{12}$. Evaporate to dryness, and test a little of the residue before the blowpipe flame on a borax bead.
A blue bead in both flames.
Presence of Co.</td></tr>
</table>

METALS OF GROUP IIIA.

addition of a few small crystals of $\left\{\begin{matrix}\mathbf{O}\text{Cl}\\ \mathbf{O}\text{Ko}\end{matrix}\right.$. Digest at a gentle heat, as long as any chlorous odour $\mathbf{C}\text{OBao}''$ and shake well. Allow to subside in a flask kept corked, to exclude the air as much as

PRECIPITATE.—Dissolve in dilute HCl; remove $\mathbf{Ba}\text{Cl}_2$ by dilute $\mathbf{S}\text{O}_2\text{Ho}_2$ and filter. Nearly neutralize the filtrate with $\mathbf{C}\text{ONao}_2$, and add pure NaHo (free from alumina) in excess and boil for a few minutes.

PRECIPITATE.—Fuse with fusion-mixture and $\mathbf{N}\text{O}_2\text{Ko}$ on platinum foil. Dissolve in hot water and filter.		**SOLUTION.**—Acidulate with dilute HCl and add AmHo in slight excess. White gelatinous precipitate. **Presence of Al.**
RESIDUE.—Dissolve in dilute HCl and add K_4FeCy_6. A precipitate of Prussian blue. **Presence of Fe.** Test the original HCl solution specially for Fe″ and Fe^{iv} by means of $\mathbf{Mn}_2\text{O}_6\text{Ko}_2$, in a highly dilute solution, as well as by means of K_4FeCy_6, $K_6Fe_2Cy_{12}$, or CyAms.	**SOLUTION**, yellow. Confirm by adding $\left\{\begin{matrix}\mathbf{C}\text{H}_3\\ \mathbf{C}\text{OHo}\end{matrix}\right.$ and $\left(\left\{\begin{matrix}\mathbf{C}\text{H}_3\\ \mathbf{C}\text{O}\end{matrix}\right.\right)_2\text{Pbo}''$. Yellow precipitate of $\mathbf{Cr}\text{O}_2\text{Pbo}''$. **Presence of Cr.** Test the original substance specially for $\mathbf{Cr}_2\text{O}_3$ and $\mathbf{Cr}\text{O}_3$, by boiling a small portion with $\mathbf{C}\text{ONao}_2$. The filtrate contains the chromate, and the residue the $\mathbf{Cr}_2\text{O}_3$. The latter may be converted into a soluble alkaline chromate by fusion with $\mathbf{C}\text{ONao}_2$ and $\mathbf{N}\text{O}_2\text{Ko}$.	

TABLE III B.—SEPARATION OF THE

B. $\mathbf{POHo_3}$ is present.—Dissolve the precipitate in dilute HCl, with the addition of a few crystals Filter off sulphur, if necessary (Note 1). Nearly neutralize with a dilute solution of $\mathbf{CONao_2}$; is produced. Heat gently, and filter hot.

<table>
<tr><td colspan="4">SOLUTION.—Add $\mathbf{Fe_2Cl_6}$ (Note 2), drop by drop, as long as a precipitate forms and till the colour of the supernatant fluid becomes red. Digest for some time at a gentle heat; allow to subside and filter hot. Wash with hot water.</td></tr>
<tr><td colspan="3">SOLUTION.—Add AmCl, AmHo and $\mathbf{SAm_2}$. A black precipitate is obtained. Filter.</td><td rowspan="3">The PRECIPITATE consists of $\mathbf{P_2O_2Fe_2o^{vi}}$ and ferric acetate. Neglect.</td></tr>
<tr><td colspan="2">SOLUTION.—Add $\mathbf{COAmo_2}$.</td><td rowspan="2">Examine PRECIPITATE according to Table IIIA for Co, Ni, Mn, Zn, Al and Cr.
Test a portion of the original substance, dissolved in water or HCl, for Fe″ and Fe^{iv}.</td></tr>
<tr><td>A white PRECIPITATE which may be—
$\mathbf{COBao''}$,
$\mathbf{COSro''}$,
$\mathbf{COCao''}$.
Examine by Table IV (without, however, mixing it with the precipitate obtained in Group IV).</td><td>SOLUTION may contain Mg. Add $\mathbf{POHoNao_2}$.
White crystalline precipitate.
Presence of Mg (as phosphate).</td></tr>
</table>

Note 1.—Test a portion of this hydrochloric acid solution with ammonic molybdate for Ca, Mg, were originally present, but only phosphates of Ni, Co, Mn, Zn and Fe, decomposable by

Note 2.—If $\mathbf{Fe_2Cl_6}$ produces no further precipitate with *a portion* of the acetic acid solution, need be added to the *main portion* of the solution.

Note 3.—Instead of fusing with $\mathbf{SiO_2}$ and $\mathbf{CONao_2}$, the presence of $\mathbf{P_2O_2Al_2o^{vi}}$ ($\mathbf{P_2O_2Cr_2o^{vi}}$ with NaHo, which dissolves $\mathbf{P_2O_2Al_2o^{vi}}$ and decomposes the ferric phosphate, with formation of reprecipitated.

METALS OF GROUP IIIB.

of $\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}Ko\end{matrix}\right.$, if necessary. Digest at a gentle heat, as long as any chlorous odour is perceptible.

then add a solution of $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}ONao\end{matrix}\right.$ and $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$ (comp. Reagents, Appendix I), as long as a precipitate

The PRECIPITATE may consist of $\mathbf{P}_2O_2Fe_2o^{vi}$, $\mathbf{P}_2O_2Al_2o^{vi}$ (Note 3), $\mathbf{P}_2O_2Cr_2o^{vi}$. Dry on the filter. Fuse in a platinum crucible with $\mathbf{Si}O_2$ and pure fusion mixture, together with a little $\mathbf{N}O_2Ko$. Dissolve in hot water, add $\mathbf{C}OAmo_2$; digest, allow to subside and filter.

<table>
<tr>
<td colspan="3">RESIDUE may consist of $\mathbf{Si}Ho_4$, $\mathbf{Si}_3O_3Fe_2o^{vi}$, $\mathbf{Si}_3O_3Al_2o^{vi}$ and $\mathbf{Fe}_2Ho_6$. Acidulate with HCl; evaporate to dryness and ignite gently. Extract with a few drops of concentrated HCl and hot water. Filter.</td>
<td rowspan="3">SOLUTION.—Add $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$ and $\left(\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}O\end{matrix}\right.\right)_2Pbo''$.
Yellow precipitate. Presence of $\mathbf{Cr}O_3$, and therefore
Presence of Cr (<i>as phosphate</i>).
A white precipitate of $\mathbf{P}_2O_2Pbo''_3$ indicating the presence of $\mathbf{P}OHo_3$, may be neglected.</td>
</tr>
<tr>
<td colspan="2">SOLUTION.—Nearly neutralize with $\mathbf{C}ONao_2$, and add pure NaHo in excess. Heat and filter.</td>
<td rowspan="2">RESIDUE $\mathbf{Si}O_2$. Neglect.</td>
</tr>
<tr>
<td>RESIDUE.—$\mathbf{Fe}_2Ho_6$. Confirm by dissolving in HCl and adding CyAms. A blood-red colour.
Presence of Fe (<i>as phosphate</i>).</td>
<td>SOLUTION.—Acidulate with dilute HCl and add AmHo in slight excess. A white gelatinous precipitate.
Presence of Al (<i>as phosphate</i>).</td>
</tr>
</table>

phosphoric acid. The absence of a yellow precipitate proves that no phosphates of Al, Cr, Ba, Sr, $\mathbf{S}Am_2$. Proceed, therefore, to examine the solution at once by Table IIIA.

it is obvious that no phosphates of the alkaline earthy bases are left, in which case no ferric salt

is rarely met with) may also be ascertained by boiling the precipitated phosphates of Fe and Al, $\mathbf{Fe}_2Ho_6$. Filter. Acidulate the filtrate with dilute HCl; add AmHo, when $\mathbf{P}_2O_2Al_2o^{vi}$ is

TABLE IV.—SEPARATION OF THE METALS OF GROUP IV.

<table>
<tr><td colspan="3">The precipitate may consist of $\mathbf{C}\mathrm{OBao}''$, $\mathbf{C}\mathrm{OSro}''$, $\mathbf{C}\mathrm{OCao}''$. Dissolve in a small quantity of dilute HCl. Evaporate to dryness on a water-bath. Pulverize the residuary chlorides (in the evaporating dish) with a pestle, and digest with absolute alcohol. Filter off through a small filter and wash with absolute alcohol.</td></tr>
<tr><td rowspan="2">RESIDUE.—$\mathbf{Ba}\mathrm{Cl}_2$.
Confirm by dissolving in water and adding $2\mathrm{HF}, \mathbf{Si}\mathrm{F}_4$ or $\mathbf{Cr}\mathrm{O}_2\mathrm{Ko}_2$.

Presence of Ba.</td><td colspan="2">SOLUTION.—Add dilute $\mathbf{S}\mathrm{O}_2\mathrm{Ho}_2$ and filter. Digest the precipitated strontic and calcic sulphates at a gentle heat for some time, with a concentrated solution of $\mathbf{S}\mathrm{O}_2\mathrm{Amo}_2$ and a little AmHo, and filter.</td></tr>
<tr><td>RESIDUE.—$\mathbf{S}\mathrm{O}_2\mathrm{Sro}''$.
Confirm by treating with concentrated HCl and heating on the loop of a platinum-wire in a Bunsen gas flame.

Presence of Sr.</td><td>SOLUTION contains $\mathbf{S}\mathrm{O}_2\mathrm{Cao}''$.
Dilute with much water, and add $\left\{\begin{matrix}\mathbf{C}\mathrm{OAmo}\\ \mathbf{C}\mathrm{OAmo}\end{matrix}\right.$, a white precipitate.

Presence of Ca.</td></tr>
</table>

TABLE V.—SEPARATION OF THE METALS OF GROUP V.

<table>
<tr><td colspan="4">The solution may contain $\mathbf{Mg}O$, $\mathbf{O}K_2$, $\mathbf{O}Na_2$ (Note 1). Evaporate to dryness and ignite in a platinum crucible, until no more ammoniacal fumes come off.</td></tr>
<tr><td rowspan="3">Dissolve a small portion of the residue in water with the aid of a few drops of HCl, and filter, if necessary. To the clear filtrate add AmCl, AmHo, and $\mathbf{P}OHoNao_2$; digest for some time at a gentle heat; stir well with a glass rod, and allow to stand for some time.
A white crystalline precipitate of $\mathbf{P}OAmoMgo''$ (Note 2).
Presence of Mg.</td><td colspan="3">Dissolve the main portion of the residue in water and a little dilute HCl; warm gently and add $\mathbf{Ba}Ho_2$, drop by drop, as long as a precipitate of $\mathbf{Mg}Ho_2$ is formed, and filter.</td></tr>
<tr><td rowspan="2">Residue.—$\mathbf{Mg}Ho_2$.
Neglect.</td><td colspan="2">Solution.—Remove excess of $\mathbf{Ba}Ho_2$ and $\mathbf{Ba}Cl_2$ by the addition of a little $\mathbf{C}OAmo_2$. Heat gently, and filter.</td></tr>
<tr><td>Residue.—$\mathbf{C}OBao''$.
Neglect.</td><td>Solution.—Evaporate to dryness, and ignite. Test the residue on platinum wire, after moistening with water, in the inner blowpipe flame.
Yellow flame.
Presence of Na.
Reddish-violet flame when seen through indigo prism, or through blue glass.
Confirm by adding $\mathbf{Pt}Cl_4$.
Presence of K.</td></tr>
</table>

Note 1.—Ammonic compounds are detected during the preliminary examination.

Note 2.—A slight *flocculent* precipitate is sometimes obtained, due to aluminic phosphate (from Al, dissolved in excess of AmHo in Group III).

EXAMINATION FOR ACIDS.

Before proceeding to the examination for acids, the analyst will do well to consider carefully which acids can possibly be combined with the bases present. A perusal of the Table of Solubility of Salts, given in the Appendix, will materially aid him, and will probably save him much labour and time.

Some acids are detected on examining for bases, viz., $\mathbf{As}_2O_3$, $\mathbf{As}_2O_5$, $\mathbf{Si}O_2$, and $\mathbf{P}OHo_3$, in combination with metals of Group III and IV, $\mathbf{Cr}O_2Ho_2$, $\mathbf{C}O_2$, $\mathbf{S}H_2$, $\mathbf{S}OHo_2$, $\mathbf{S}SOHo_2$, ClHo, $\mathbf{N}OHo$, the six lastly mentioned acids on dissolving the substance in dilute HCl, or on adding HCl in Group I.

A careful preliminary examination for acids will probably lead to the detection of a further number of acids, *e.g.*, of HI, $\left\{\begin{matrix}\mathbf{O}I\\ \mathbf{O}Ho\end{matrix}\right.$, HBr, $\left\{\begin{matrix}\mathbf{O}Br\\ \mathbf{O}Ho\end{matrix}\right.$, and $\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}Ho\end{matrix}\right.$, $\mathbf{N}O_2Ho$ ($\mathbf{N}OHo$), HCl, (ClHo), HF, HCy, H_4FeCy_6, $H_6Fe_2Cy_{12}$, CyHo and CyHs, $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$ and $\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right.$. The presence of other organic acids is likewise indicated. When more than one of these acids is present, the detection is somewhat more difficult, and the results obtained by a preliminary examination for acids require to be carefully confirmed by the examination of the solution. Thus a chloride in the presence of a nitrate, when treated with concentrated $\mathbf{S}O_2Ho_2$, evolves chlorine and red fumes of lower oxides of nitrogen, in the presence of a chromate, brownish-red fumes of $\mathbf{Cr}O_2Cl_2$. $\mathbf{Hg}Cl_2$, $\mathbf{Hg}_2Cl_2$, or $\mathbf{Sn}Cl_4$ does not evolve HCl when treated with $\mathbf{S}O_2Ho_2$. Sulphides, when treated with HCl, often evolve $\mathbf{S}H_2$, with separation of sulphur. $\mathbf{S}O_2$ and $\mathbf{S}H_2$, when evolved simultaneously, destroy each other, etc.

When the preliminary examination gives no distinct indication of the presence of any of the acids just mentioned, $\mathbf{S}O_2Ho_2$, $\mathbf{B}Ho_3$, $\mathbf{P}OHo_3$, $\mathbf{Si}O_2$ will have to be looked for.

The analyst will have to bear in mind that acids cannot be detected in the same systematic order as bases, and that he ought, therefore, never to be satisfied till he has confirmed the presence of acids by the most characteristic *special* tests.

PRELIMINARY EXAMINATION FOR ACIDS.

Experiment.	Observation.	Inference.
TREAT A LITTLE OF THE POWDERED SUBSTANCE IN A TEST-TUBE WITH DILUTE HCl, AND HEAT GENTLY.	Certain acids are given off 1. WITHOUT DECOMPOSITION.	
	A colourless and inodorous gas is evolved, which precipitates lime- or baryta-water	$\mathbf{C}O_2$, from carbonates, likewise from cyanide and cyanates containing carbonates.
Confirm by passing $\mathbf{S}O_2$ through an acidulated solution of $\mathbf{Cr}O_2Ko_2$	A gas is evolved, having the odour of burning sulphur	$\mathbf{S}O_2$, from sulphites.
Test the gas with lead-paper	A gas is given off, possessing a most fœtid odour—the odour of rotten eggs	$\mathbf{S}H_2$, from metallic sulphides (with the exception of $\mathbf{Cu}S$, $\mathbf{S}Ag_2$, $\mathbf{Bi}_2S_3$, $\mathbf{Hg}S$, $\mathbf{Pt}S_2$, $\mathbf{Au}_2S_3$, and $\mathbf{As}_2S_3$).
	Reddish-brown fumes	$\mathbf{N}_2O_3$, from nitrites.
	A colourless gas, possessing the odour of bitter almonds	HCy, from cyanides.
	2. WITH DECOMPOSITION.	
	A yellowish-green gas, of suffocating odour, bleaching vegetable colours	Cl, from hypochlorites, also from decomposition of $\mathbf{Cr}O_2Ho_2$ and HCl.
	$\mathbf{S}O_2$ is evolved, and yellow sulphur is precipitated	From hyposulphites.
	$\mathbf{C}O_2$ is given off, accompanied by the pungent odour of CyHo. AmCl being formed at the same time, and the residue gives off $\mathbf{N}H_3$ when heated with $\mathbf{Ca}Ho_2$	From decomposition of cyanates.
HEAT ANOTHER PORTION OF THE SOLID SUBSTANCE WITH MODERATELY CONCENTRATED $\mathbf{S}O_2Ho_2$	Certain acids are given off .. 1. WITHOUT DECOMPOSITION.	$\mathbf{C}O_2$, $\mathbf{S}O_2$, $\mathbf{S}H_2$, $\mathbf{N}_2O_3$, HCy (already recognized on treating with dilute HCl).
	$\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$ is given off	$\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$
Confirm by distilling with EtHo and concentrated $\mathbf{S}O_2Ho_2$	$\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OEto\end{matrix}\right.$ is given off	$\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$

PRELIMINARY EXAMINATION FOR ACIDS—*continued.*

Experiment.	Observation.	Inference.
	Pungent acid fumes	HCl, HF, HCy.
	2. WITH DECOMPOSITION	$\mathbf{S}SOHo_2$, ClHo, CyHo (already noticed).
	A gas is evolved, possessing the odour of bitter almonds	HCy (from ferro- and ferricyanides).
Confirm by causing the gas to act upon $\mathbf{S}Am_2$, and adding $\mathbf{Fe}_2Cl_6$.	Blood-red colouration	Cyanogen compounds.
TREAT A LITTLE OF THE SUBSTANCE WITH CONCENTRATED $\mathbf{S}O_2Ho_2$, AND WARM GENTLY (not sufficiently, however, to volatilize the $\mathbf{S}O_2Ho_2$).	Certain acids are given off— 1. WITHOUT DECOMPOSITION..............	$\mathbf{N}O_2Ho$, HCl, HCy, HF, $\bar{B}zHo$, $\bar{S}uHo_2$.
Confirm HCl by heating with $\mathbf{Mn}O_2$ and $\mathbf{S}O_2Ho_2$.	Cl gas is evolved, recognized by its odour, its action upon vegetable colours, and upon KI and starch paste	HCl.
Confirm HF by etching on glass.	Heavy suffocating fumes, which corrode glass	HF.
Confirm $\mathbf{N}O_2Ho$ by adding concentrated $\mathbf{S}O_2Ho_2$ to a solution of the salt, and $\mathbf{S}O_2Feo''$. If a chlorate as well as a nitrate be present, ignite previous to treating with $\mathbf{S}O_2Ho_2$ and $\mathbf{S}O_2Feo''$.	A brown ring is formed	$\mathbf{N}O_2Ho$.
	2. WITH DECOMPOSITION	ClHo and CyHo (already noticed), $\mathbf{S}H_2$, HI, HBr, $\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}Ho\end{matrix}\right.$, $\left\{\begin{matrix}\mathbf{O}Br\\ \mathbf{O}Ho\end{matrix}\right.$, $\mathbf{Cr}O_2Ho_2$, formic, tartaric and citric acids, $\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right.$, CyHs, H_4FeCy_6, $H_6Fe_2Cy_{12}$.
	$\mathbf{S}H_2$, as well as $\mathbf{S}O_2$, are evolved, owing to the action of the liberated sulphur upon $\mathbf{S}O_2Ho_2$.	Metallic sulphides.

	Oxygen is given off, and the yellow chromate is changed into green chromic sulphate	CrO_2Ho_2.
	Chloric peroxide a greenish-yellow, highly explosive gas is given off	$\left\{\begin{matrix}OCl\\OHo\end{matrix}\right.$.
	Detonation in the test-tube on the application of heat	
Confirm HBr and HI by distilling with MnO_2 and concentrated SO_2Ho_2.	Bromine is evolved (together with HBr and SO_2), which condenses to a reddish-brown liquid: the gas colours starch paste yellow	HBr and $\left\{\begin{matrix}OBr\\OHo\end{matrix}\right.$.
	Iodine is given off; violet fumes and sublimate colouring starch paste blue	HI.
	Chlorine is evolved	HCl, in the presence of CrO_2Ho_2.
	Chlorine and nitrous fumes are given off	HCl, together with NO_2Ho or $NOHo$.
	CO is given off, without blackening	Formic acid.
	The substance blackens, owing to separation of carbon, with evolution of CO, CO_2, and SO_2, and gives off the characteristic odour of burnt sugar	$\left\{\begin{matrix}COHo\\CHHo\\CHHo\\COHo\end{matrix}\right.$ and $\left\{\begin{matrix}CHHo(COHo)\\CH(COHo)\\CH_2(COHo)\end{matrix}\right.$.
Pass gases through a solution of NaHo. The CO burns with a blue flame.	CO and CO_2 are evolved without blackening	Oxalic acid.
	The acid is decomposed into CO and NH_3, the latter remaining combined with the acid	Cyanides, ferro- and ferricyanides.
	CO_2 is given off, and ammonic sulphate is left	Cyanates.
	CO_2 and SH_2 are evolved with separation of sulphur, which reacts upon the SO_2Ho_2 and forms SO_2, ammonic sulphate being left	Sulphocyanates.
	No gas or vapour is evolved	SiO_2, BHo_3, $POHo_3$, SO_2Ho_2, $AsOHo_3$, $\left\{\begin{matrix}OI\\OHo\end{matrix}\right.$.
	A gelatinous mass or a flaky powder is left ..	$SiHo_4$ from soluble silicates, or from silicates decomposable by acids.
	Scaly crystals separate, possessing a pearly lustre	BHo_3.

PREPARATION OF SOLUTIONS FOR ACIDS.

Great care ought to be bestowed upon the preparation of the solutions required for the examination of acids. On boiling a portion of the substance under examination with $\mathbf{C}ONao_2$ nearly all the metals, other than alkalies, are precipitated in the form of carbonates, basic carbonates, or oxides.

(It is necessary to decompose the salts first in order to prevent the precipitation by the several reagents employed for the detection of acids in the wet way, *e.g.*, of Ba, Sr, Ca, or Pb, on the addition of $\mathbf{S}O_2Cao''$ or $\mathbf{S}O_2Mgo''$; of Ag, $'Hg'_2$ or Pb, by $\mathbf{Ba}Cl_2$ or $\mathbf{Ca}Cl_2$; of Fe and others by AmHo, etc., etc.)

The precipitate produced by $\mathbf{C}ONao_2$ (which reagent ought to be added in the least possible excess) is filtered off, and the filtrate tested with a few more drops of $\mathbf{C}ONao_2$. If no further precipitation takes place the solution is heated to boiling, and

1. Dilute HCl added to a portion of it, as long as $\mathbf{C}O_2$ is evolved, and till the solution is rendered distinctly acid.

(Small quantities of $\mathbf{S}O_2Nao_2$ and NaCl are almost invariably contained in the commercial $\mathbf{C}ONao_2$; it is therefore necessary to test a portion of the aqueous or HCl solution of the substance, prepared without the intervention of $\mathbf{C}ONao_2$, for $\mathbf{S}O_2Ho_2$ by means of $\mathbf{Ba}Cl_2$. A $\mathbf{N}O_2Ho$ solution of the original substance is in like manner tested for HCl by adding $\mathbf{N}O_2Ago$.)

2. Another portion of the alkaline filtrate is rendered acid by means of dilute $\mathbf{N}O_2Ho$ and boiling.

3. A third portion is rendered acid by means of dilute $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$; and lastly—

4. A fourth portion of the alkaline solution is *carefully neutralized* by first adding dilute $\mathbf{N}O_2Ho$, drop by drop, and boiling, as long as $\mathbf{C}O_2$ is evolved and till the solution is distinctly acid to test-paper: then by adding a few drops of very dilute AmHo, till the solution gives a neutral reaction with blue and red litmus-papers. *The strictest attention should be paid to these directions*, and the least possible excess of either acid or alkali should be employed, since the precipitation of several acids is prevented by the formation of an ammonic salt in anything like large quantities, on account of the formation of a soluble double salt, *e.g.*, ammonic calcic tartrate, ammonic calcic citrate, etc., etc.

If the preliminary examination for bases has shown the presence of ammonic salts, it is necessary to decompose them by boiling with caustic NaHo, before preparing Solution IV.

Ebullition or fusion with $\mathbf{C}ONao_2$ decomposes the phosphates of the alkaline earths but very imperfectly, and the phosphoric acid so combined is invariably detected by means of $\mathbf{Mo}O_2Amo_2$. (Comp. Table III B.)

If organic acids are present in combination with heavy metals (viz., those of Groups I and II), $\mathbf{S}H_2$ should be passed through the slightly acid (HCl) solution and the precipitate filtered off. The solution is freed from $\mathbf{S}H_2$ by boiling, then rendered slightly alkaline by means of a few drops of NaHo and tested by means of $\mathbf{Ca}Cl_2$ (ammonic salts should be carefully avoided).

No further notice need be taken of the following acids: $\mathbf{C}O_2$, $\mathbf{S}H_2$, $\mathbf{S}O_2$, $\mathbf{N}OHo$, ClHo, $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$, since they can be detected with certainty by a preliminary examination, and as they would, for the most part, be lost on acidulating the solutions.

PORTION ACIDULATED WITH HCl.

$\mathbf{S}O_2Ho_2$.—On the addition of $\mathbf{Ba}Cl_2$ a white precipitate insoluble on boiling.

$\mathbf{Si}Ho_4$.—On the addition of AmCl or $\mathbf{C}OAmo_2$ a gelatinous precipitate, requiring no further confirmation, since $\mathbf{Si}O_2$ is left on evaporating the filtrate from Group II with $\mathbf{N}O_2Ho$.

H_4FeCy_6.—On the addition of $\mathbf{Fe}_2Cl_6$ a deep blue precipitate.
,, ,, $\mathbf{S}O_2Feo''$ light ,, ,,
$H_6Fe_2Cy_{12}$.— ,, ,, ,, dark deep ,, ,,
,, ,, $\mathbf{Fe}_2Cl_6$ a brown coloration only.
If both acids are present, filter off, after adding $\mathbf{Fe}_2Cl_6$, and observe the colour of the filtrate. On the addition of $\mathbf{Sn}Cl_2$ or $\mathbf{S}OHo_2$ to the filtrate a blue precipitate is immediately obtained, confirmatory of the presence of $H_6Fe_2Cy_{12}$.

CyHs.—$\mathbf{Fe}_2Cl_6$ produces a blood-red coloration, which is destroyed by $\mathbf{Hg}Cl_2$ and not by HCl (the red colour which $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$ imparts to a solution of $\mathbf{Fe}_2Cl_6$ is destroyed by HCl).

2HF, $\mathbf{Si}F_4$.—On the addition of $\mathbf{Ba}Cl_2$ a gelatinous translucent precipitate of $\mathbf{Ba}F_2,\mathbf{Si}F_4$ is obtained, which is decomposed by strong acids. Confirm by heating the precipitate, when volatile $\mathbf{Si}F_4$ is given off. AmHo precipitates gelatinous $\mathbf{Si}Ho_4$ with formation of AmF, $\mathbf{Ba}F_2$ and $\mathbf{O}H_2$.

PORTION ACIDULATED WITH $\mathbf{N}O_2Ho$.

HCl.—On the addition of $\mathbf{N}O_2Ago$ a white curdy precipitate, soluble in AmHo. For the distinction between *hydrochloric and chloric acids* comp. p. 249.

HBr.—On the addition of $\mathbf{N}O_2Ago$ a yellowish-white precipitate, difficultly soluble in AmHo. Confirm by adding chlorine water to the original solution, and shake up with ether. Bromine dissolves to a yellowish-red liquid.

$\left\{\begin{matrix}\mathbf{O}Br\\ \mathbf{O}Ho\end{matrix}\right.$.—On the addition of $\mathbf{N}O_2Ago$ a white amorphous precipitate, little soluble in water and dilute $\mathbf{N}O_2Ho$, easily soluble in AmHo.—AgBr and $\left\{\begin{matrix}\mathbf{O}Br\\ \mathbf{O}Ago\end{matrix}\right.$ may be separated by washing with water. Argentic bromate being soluble may be detected in the solution by the addition of $\mathbf{S}OHo_2$, when a precipitate of AgBr is obtained.

For *the distinction between HBr and HCl*, comp. page 253.

HI.—On the addition of $\mathbf{N}O_2Ago$ a yellow precipitate, scarcely soluble in AmHo. Confirm by the blue colour imparted to starch paste by the iodine liberated by $\mathbf{N}_2O_3$ gas.

$\left\{\begin{matrix}\mathbf{O}I\\ \mathbf{O}Ho\end{matrix}\right.$.—On the addition of $\mathbf{N}O_2Ago$ a white precipitate of $\left\{\begin{matrix}\mathbf{O}I\\ \mathbf{O}Ago\end{matrix}\right.$, insoluble in dilute $\mathbf{N}O_2Ho$, soluble in AmHo (AgI is insoluble), whence AgI is precipitated on the addition of $\mathbf{S}OHo_2$. On adding $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$ to a mixture of an iodide and iodate the former is instantly decomposed, iodine being set free,—most readily recognized by the delicate iodide of starch reaction.

Distinction between HCl and HI.—HCl in the presence of HI cannot be distinguished in the same ready manner as HCl in the presence of HBr. The two acids are precipitated by $\mathbf{N}O_2Ago$. The precipitate is digested with AmHo and filtered, AgI being insoluble in AmHo. Dilute $\mathbf{N}O_2Ho$ reprecipitates white AgCl from the filtrate.

Distinction between HCl, HBr and HI.—Precipitate the HI as $\mathbf{Cu}_2I_2$ by means of $\mathbf{S}O_2Cuo''$ and $\mathbf{S}O_2Feo''$ or $\mathbf{S}OHo_2$, and filter. Remove the cupric and ferric salts by a little pure KHo, evaporate the filtrate to dryness, and examine for HCl and HBr by testing one portion for HCl with $\mathbf{Cr}_2O_5Ko_2$ and $\mathbf{S}O_2Ho_2$, and another for HBr by chlorine-water and ether.

HCy.—On the addition of $\mathbf{N}O_2Ago$ a white curdy precipitate soluble in AmHo and alkaline cyanides.

In order *to distinguish* HCy *in the presence of* HCl, filter off precipitate, wash well and ignite in a porcelain crucible to red heat. Dissolve the metallic Ag left by the decomposition of AgCy with a little hot $\mathbf{N}O_2Ho$, and test the clear solution with HCl. A curdy white precipitate indicates HCy. Confirm also by the reaction with ferroso-ferric salts, KHo and HCl in a fresh portion of the solution.

Distinction between HCl, HBr, HI, and HCy.—Test specially for HCy, before proceeding to the examination of the other acids as described, by treating a small quantity of the mixed salts in a porcelain dish with very dilute $\mathbf{S}O_2Ho_2$, and causing the evolved HCy to act upon a drop of $\mathbf{N}O_2Ago$, or a little $\mathbf{S}Am_2$, contained in a second porcelain dish, inverted over the one containing the mixed salts. A white precipitate of AgCy is obtained; or the CyAms which is formed gives a blood-red colour with ferric salts, affording equally conclusive evidence of the presence of HCy.

$\left.\begin{matrix}CyHs\\ H_4FeCy_6\\ H_6Fe_2Cy_{12}\end{matrix}\right\}$ are likewise precipitated on the addition of $\mathbf{N}O_2Ago$, and are insoluble in dilute $\mathbf{N}O_2Ho$. The first and second form salts which are insoluble in AmHo, whilst $Ag_6Fe_2Cy_{12}$ is readily soluble. These acids are, however, best detected in the portion acidulated with HCl.

No other cyanogen compound but a cyanide gives off HCy when treated with very dilute $\mathbf{S}O_2Ho_2$, and it is therefore possible, also, to distinguish HCy in the presence of CyHs, CyHo, H_4FeCy_6, $H_6Fe_2Cy_{12}$.

PORTION ACIDULATED WITH $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$.

HF.—On the addition of $\mathbf{Ca}Cl_2$ a white gelatinous precipitate. $\mathbf{S}O_2Ho_2$ is likewise precipitated by $\mathbf{Ca}Cl_2$ in an acetic acid solution: it is therefore necessary invariably to test specially for HF, by etching on glass.

$\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right.$.—On the addition of $\mathbf{S}O_2Cao''$ a white precipitate of $\left\{\begin{matrix}\mathbf{C}O\\ \mathbf{C}O\end{matrix}\right.Cao''$ is obtained, which on ignition leaves $\mathbf{C}OCao''$, soluble with effervescence in $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$. (Calcic fluoride is not affected.)

$\mathbf{Cr}O_2Ho_2$.—On the addition of plumbic acetate a yellow precipitate.

$\mathbf{P}OHo_3$.—On the addition of $\mathbf{Fe}_2Cl_6$ a yellowish-white gelatinous precipitate from a solution of a soluble phosphate, or a phosphate decomposable by boiling with $\mathbf{C}ONao_2$. Arsenic acid, if present, should be first removed by means of $\mathbf{S}H_2$.

PORTION RENDERED NEUTRAL.

$\bar{T}Ho_2$.—On the addition of $\mathbf{Ca}Cl_2$ a white precipitate, soluble in AmCl or cold KHo.—$\mathbf{S}O_2Ho_2$, $\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right.$, HF,

$\mathbf{P}\mathrm{OHo}_3$, $\mathbf{As}\mathrm{OHo}_3$, $\mathbf{B}\mathrm{Ho}_3$, $\mathbf{Si}\mathrm{Ho}_4$, $\mathbf{C}\mathrm{O}_2$, $\mathbf{S}\mathrm{OHo}_2$, are likewise precipitated by $\mathbf{Ca}\mathrm{Cl}_2$ from a neutral solution, and $\overline{\mathrm{T}}\mathrm{Ho}_2$ can obviously be detected only by further special tests in the presence of any of these acids. The most characteristic reaction consists in warming some $\overline{\mathrm{T}}\mathrm{Ago}_2$, dissolved in very little dilute AmHo, in a water-bath, until a bright mirror of metallic silver is obtained.

$\overline{\mathrm{Ci}}\mathrm{Ho}_3$.—On the addition of $\mathbf{Ca}\mathrm{Cl}_2$ no precipitate is obtained, till excess of AmHo, or $\mathbf{Ca}\mathrm{Ho}_2$, has been added and the solution boiled.

The detection of tartaric and citric acids—indicated during the preliminary examination by a strong odour of burnt sugar—requires great care and strict attention to the few points of distinction which exist between them. The precipitate produced by $\mathbf{Ca}\mathrm{Cl}_2$ in the cold should be filtered off, and the filtrate tested for $\overline{\mathrm{Ci}}\mathrm{Ho}_3$, by adding a drop of AmHo and boiling, when a fresh precipitate of calcic citrate is obtained. $\overline{\mathrm{Ci}}\mathrm{Ago}_3$ dissolved in dilute AmHo, forms a less lustrous mirror, and only after boiling for a long time.

$\mathbf{B}\mathrm{Ho}_3$.—$\mathbf{Ca}\mathrm{Cl}_2$ produces from a concentrated solution of a borate a whitish precipitate soluble in AmCl. $\mathbf{B}\mathrm{Ho}_3$ is also indicated in the preliminary examination by the swelling up of some of its saline compounds, and the precipitation of a concentrated solution of a borate with concentrated $\mathbf{S}\mathrm{O}_2\mathrm{Ho}_2$ or HCl.

More delicate, however, is the reaction which boric acid gives with turmeric paper, and the colour which boric fluoride imparts to the flame. (Comp. page 272 and 273.)

$\overline{\mathrm{Bz}}\mathrm{Ho}$.—On the addition of $\mathbf{Fe}_2\mathrm{Cl}_6$ a pale yellow precipitate. Confirm by the reactions which a benzoate gives in the preliminary examination, since a precipitate of $\mathbf{Fe}_2\mathrm{Ho}_6$ is frequently mistaken for ferric benzoate, owing to imperfect neutralization.

$\overline{\mathrm{Su}}\mathrm{Ho}_2$.—On the addition of $\mathbf{Fe}_2\mathrm{Cl}_6$ a reddish brown precipitate.

For *the distinction between benzoic and succinic acids*, compare page 293.

APPENDIX I.

REAGENTS.

SOLVENTS.

DISTILLED WATER.*

Obtained by condensing steam by means of a tin worm. The first portions of the condensed water usually contain carbonic anhydride and ammonic carbonate, and should be rejected.

Impurities.—When evaporated in a platinum vessel, distilled water should not leave a solid residue, either organic or mineral. $\mathbf{S}\text{Am}_2$ ought not to give a precipitate (Cu, Pb, Fe), neither ought basic plumbic acetate to cause a turbidity ($\mathbf{C}\text{O}_2$, $\mathbf{C}\text{OAmo}_2$). No turbidity or precipitate should be produced, moreover, on the addition of $\left\{\begin{matrix}\mathbf{C}\text{OAmo}\\ \mathbf{C}\text{OAmo}\end{matrix}\right.$ (lime), $\mathbf{Ba}\text{Cl}_2$ (sulphates), or $\mathbf{N}\text{O}_2\text{Ago}$ (chlorides). Pure distilled water is colourless, inodorous, and tasteless.

Water used for Nessler's test should be specially distilled in a glass retort with a few pieces of caustic potash, and the distillate rejected as long as the Nessler solution indicates any ammonia.

ALCOHOL (METHYLATED SPIRIT), $\mathbf{C}_2\text{H}_5\text{Ho}$ or EtHo.

Ordinary methylated spirit (*i.e.*, ethylic alcohol, 90 p.c., mixed with 10 p.c. of wood spirit or methylic alcohol) may be employed for most purposes. It can be rendered absolute by shaking with well dried potassic carbonate and distilling the clear spirit in a flask or retort from a water-bath.

Impurities.—Commercial methylated spirit frequently leaves a residue on evaporation, if so, it should be rectified by distillation. It should not redden blue litmus paper.

ETHER, $\left\{\begin{matrix}\mathbf{C}_2\text{H}_5\\ \text{O}\\ \mathbf{C}_2\text{H}_5\end{matrix}\right. = \mathbf{O}\text{Et}_2$.

The ordinary ether (methylated, *i.e.*, prepared from methylated alcohol) of commerce, is pure enough.

* The asterisk marks the more important reagents.

ACIDS.

SULPHURIC ACID,* SO_2Ho_2.

Common oil of vitriol may be used in all operations with which its usual impurities (lead, arsenic, iron, lime, nitric acid) do not interfere. Pure sulphuric acid, free from arsenic, should be employed for generating arsenietted or antimoniettted hydrogen, and an acid free from lead, whenever this metal has to be precipitated as sulphate. Sulphuric acid, free from nitric acid and nitric peroxide, ought to be employed in testing for nitric acid by means of ferrous sulphate.

Impurities.—Pure sulphuric acid should be colourless, and leave no residue on evaporation in a porcelain dish. When a solution of ferrous sulphate is poured upon it in a narrow test-tube, it should not form a brown ring, where the two liquids come in contact (nitric acid and nitric peroxide), nor strike a blue colour when a highly diluted solution of the acid is added to a solution of pure potassic iodide and starch paste (nitric peroxide). The presence of arsenic is best ascertained by passing a current of SH_2 through the dilute acid, or by generating hydrogen from zinc free from arsenic, and passing the gas through an ignited combustion tube (Marsh's test, Fig. 83). Plumbic sulphate is frequently found in sulphuric acid, and is precipitated on diluting with water, being less soluble in dilute than in concentrated acid. Hydrochloric acid should cause no turbidity (lead) where the two liquids meet.

The pure acid can readily be bought now, and the student should not attempt to purify the crude acid.

DILUTE SULPHURIC ACID.*

Prepared by pouring slowly one part by measure of the concentrated acid (sp. gr. 1·8) into five parts by measure of distilled water, with continuous stirring. Thin glass vessels (beakers) or a porcelain dish should be employed, as much heat is evolved. Allow the plumbic sulphate to subside, and decant or syphon off the clear liquid.

NITRIC ACID,* *Aqua fortis*, NO_2Ho.

Should be colourless, and leave no residue on evaporation in a glass dish.

Impurities.—Sulphuric and hydrochloric acids. Dilute considerably, and test portions with baric nitrate and argentic nitrate.

DILUTE NITRIC ACID.*

Prepared by diluting one part of pure commercial acid (sp. gr. 1·38 to 1·45) with three parts of distilled water.

CRUDE NITRIC ACID.*

May be employed for all experiments in which the above impurities do not interfere, *e.g.*, in the preparation of $\mathbf{N}_2O_2$ or $\mathbf{N}_2O_3$ by the action of nitric acid upon copper or arsenious anhydride.

Concentrated Hydrochloric Acid,* Muriatic Acid, HCl.

Should be colourless, and leave no residue on evaporation.

Impurities.—Ferric chloride, sulphurous and sulphuric acids, arsenic. The acid should not impart a blue colour to a solution of KI and starch paste (Cl or $\mathbf{Fe}_2Cl_6$). On adding a few drops of a solution containing iodide of starch, the blue colour should not be destroyed ($\mathbf{S}O_2$). The dilute acid should remain clear on the addition of a solution of $\mathbf{Ba}Cl_2$ ($\mathbf{S}O_2Ho_2$). Sulphuretted hydrogen, when passed through the dilute acid, should not produce a precipitate (arsenic), nor should ammonic sulphocyanate redden the diluted acid (iron).

Dilute Hydrochloric Acid.*

Pure commercial acid, sp. gr. 1·16, is diluted with three times its bulk of distilled water.

Crude Hydrochloric Acid.*

Should be employed, whenever the impurities which it contains do not interfere with the object in view, as for instance in the preparation of chlorine from $\mathbf{Mn}O_2$.

Aqua Regia or Nitrohydrochloric Acid.

Prepared, when required only, by mixing one part of concentrated nitric acid with three to four parts of hydrochloric acid.

Sulphurous Acid, $\mathbf{S}OHo_2$.

Prepared by acting with concentrated $\mathbf{S}O_2Ho_2$ upon copper, and passing the gas into water. The solution should be kept in a well stoppered bottle.

Carbonic Acid Water.

A solution is prepared by acting with HCl upon marble, and passing the evolved carbonic anhydride into water.

Chlorine Water.

A solution of chlorine in water is prepared as described, p. 46. It should be kept in a well stoppered bottle, and in a dark place, since, on exposure to light, it is speedily converted into HCl with evolution of oxygen.

Acetic Acid,* $\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}OHo\end{array}\right.$.

Pure commercial acid of sp. gr. 1·04, diluted with one part of water may be used. It should leave no residue on evaporation.

Impurities.—Sulphuric and hydrochloric acids, lead, copper, iron, lime.

TARTARIC ACID, $\left\{\begin{array}{l}\mathbf{C}\mathrm{OHo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{OHo}\end{array}\right.$.

A solution is prepared when required only, as the acid undergoes decomposition in an aqueous solution. One part by weight of commercial tartaric acid of sufficient purity is dissolved in three parts of water (*i.e.*, 1 grm. in 3 c.c. of water).

Impurities.—Tartaric acid contains sometimes gypsum and calcic tartrate, which are best tested for by igniting a few crystals on platinum, extracting the residue, if any, with a few drops of dilute HCl, and adding to one portion $\mathbf{Ba}\mathrm{Cl}_2$, to another AmHo, and $\left\{\begin{array}{l}\mathbf{C}\mathrm{OAmo}\\ \mathbf{C}\mathrm{OAmo}\end{array}\right.$.

OXALIC ACID, $\left\{\begin{array}{l}\mathbf{C}\mathrm{OHo}\\ \mathbf{C}\mathrm{OHo}\end{array}\right.$.

The commercial acid is sufficiently pure. It should not leave more than a trace of a residue on ignition.

Impurities.—Iron, potassic and sodic oxalates, lime. Dissolve one part by weight of the crystallized acid, $\left\{\begin{array}{l}\mathbf{C}\mathrm{OHo}\\ \mathbf{C}\mathrm{OHo}\end{array}\right.$, + 2 aq., in ten parts by measure of water.

HYDROFLUORIC ACID, HF.

A solution stored up in a gutta-percha bottle is best bought, as its preparation involves expensive apparatus. It should leave no fixed residue on evaporation to dryness.

HYDROFLUOSILICIC ACID, $2\mathrm{HF},\mathbf{Si}\mathrm{F}_4$.

A solution of this acid in water is prepared, as described, p. 262. It should be made sufficiently strong to precipitate a soluble baric salt readily.

Impurities.—Owing to the mode of preparation the acid is often contaminated with sulphuric acid. It should not produce a precipitate in a solution of a strontic salt ($\mathbf{S}\mathrm{O}_2\mathrm{Ho}_2$).

HYDROSULPHURIC ACID, $\mathbf{S}\mathrm{H}_2$.

Prepared, when required, as described, p. 41. In well appointed laboratories sulphuretted hydrogen is now usually stored in a gas-holder over oil, and supplied like coal gas from small taps in closets connected with the chimney. The gas, whether obtained from a generating flask (Fig. 38), or from a gas-holder, should invariably be passed through a wash-bottle containing water. A saturated solution of $\mathbf{S}\mathrm{H}_2$ in water answers most purposes of the analyst. It should be kept in a well-stoppered bottle, since sulphuretted hydrogen decomposes rapidly when in contact with air, with formation of sulphuric acid and precipitation of white sulphur.

If the gas be required entirely free from AsH_3, it should be generated by acting with pure HCl (concentrated) upon native *grey antimony*, Sb_2S_3.

BASES AND METALS.

POTASSIC HYDRATE,* KHo, OR SODIC HYDRATE, $NaHo$.

Usually obtained in commerce in the form of sticks or lumps, which may be dissolved in twenty parts of water.

Impurities.—Silica, alumina, phosphoric, sulphuric, and hydrochloric acids (sulphates and chlorides, often in not inconsiderable quantities), and carbonic acid. On dissolving in water, and allowing the suspended matter to subside, the clear solution may be syphoned off.

Pure sodic hydrate is indispensable for the separation of alumina from the oxides of iron and chromium.

AMMONIC HYDRATE,* $AmHo$.

The *liquor ammoniæ* of commerce, sp. gr. ·88, is diluted with distilled water till the liquid has a sp. gr. of ·96 = 10 per cent. of NH_3.

Impurities.—A solution of ammonia should be colourless; on neutralizing with pure HCl it should remain inodorous. When evaporated in a glass dish, it should not leave any residue. Ammonia contains frequently traces of sulphuric and hydrochloric acids, and sometimes not inconsiderable quantities of ammonic carbonate, when it produces a white precipitate on the addition of lime water.

BARIC HYDRATE,* $BaHo_2$.

Obtained by dissolving in a stoppered bottle one part of crystallized baric hydrate, $BaHo_2 + 8aq$, in twenty parts of water. Allow to subside and syphon off into another well-stoppered bottle.

Impurities.—The solution commonly called *baryta-water* should, on precipitating with pure SO_2Ho_2, give a filtrate which leaves no fixed residue on evaporating to dryness in a platinum vessel.

CALCIC HYDRATE,* $CaHo_2$.

Freshly slaked lime in powder is used in qualitative analysis, as well as a solution of lime, so-called *lime-water*. This is prepared by dissolving in *cold* distilled water some freshly slaked lime, allowing to subside in a stoppered bottle, and syphoning off the clear liquid into another bottle. Lime-water contains about 1 part of lime dissolved in 600 of water.

AMMONIC SULPHIDE,* $\mathbf{S}Am_2$.

Prepared by saturating three parts of ammonic hydrate with $\mathbf{S}H_2$ gas, whereby $\mathbf{S}HAm$ is formed. On diluting this solution of hydric ammonic sulphide with two parts of ammonic hydrate, a sulphide is obtained which contains a little free ammonia. The concentrated solution may be diluted with ten times its bulk of water. It should be kept in well-stoppered bottles. Calcic or magnesic salts should not be precipitated; nor should the solution leave a residue on evaporation and ignition. The oxygen of the air decomposes it gradually into $\mathbf{N}H_3$,$\mathbf{O}H_2$ and yellow $\mathbf{S}SAm_2$.

YELLOW AMMONIC SULPHIDE, $\mathbf{S}SAm_2$.

Used for the solution and conversion of $\mathbf{Sn}S$ into $\mathbf{Sn}S_2$. It may be prepared by digesting the neutral $\mathbf{S}Am_2$ with flowers of sulphur and filtering the liquid.

SODIC SULPHIDE, $\mathbf{S}Na_2$.

Prepared by saturating one portion of a solution of sodic hydrate with $\mathbf{S}H_2$, and adding to it the second portion. A little $\mathbf{Fe}S$, which is generally precipitated, is filtered off. The solution must be kept in a well-stoppered bottle.

SALTS.

POTASSIC SULPHATE, $\mathbf{S}O_2Ko_2$.

Dissolve one part of the commercial salt in twelve parts of water.

POTASSIC IODIDE, KI.

The commercial salt is generally sufficiently pure. Dissolve in sixty parts of water. Pure KI should be free from iodate and carbonate. It should not colour starch paste blue on the addition of dilute $\mathbf{S}O_2Ho_2$.

POTASSIC NITRITE, $\mathbf{N}OKo$.

Dissolve one part of the commercial salt in two parts of water, when required for use.

POTASSIC CHROMATE, $\mathbf{Cr}O_2Ko_2$.

Dissolve the salt of commerce in ten parts of water.

Impurities.—Sulphuric acid. The solution ought not to become turbid on the addition of dilute HCl and $\mathbf{Ba}Cl_2$.

DIPOTASSIC DICHROMATE, $\mathbf{Cr}_2O_5Ko_2$.

Purify the commercial salt by recrystallisation till it is free from $\mathbf{S}O_2Ko_2$, and dissolve one part in ten of water.

Potassic Metantimoniate, $\mathbf{Sb}O_2Ko + 5aq.$

Prepared by deflagrating in a Hessian crucible one part of finely powdered antimony with four parts of saltpetre. Pour the fused mass on a stone slab. Powder it, and boil with twelve parts of water for two or three hours, and filter, when a clear and neutral solution is obtained. KCl and AmCl should not precipitate it.

Potassic Ferrocyanide,* K_4FeCy_6, and Ferricyanide, $K_6Fe_2Cy_{12}$.

These salts can be purchased in a state of sufficient purity. They are dissolved, in small quantities at a time, in 12 parts of water.

Potassic Sulphocyanate, CyKs, or Ammonic Sulphocyanate, CyAms.

Dissolve in 10 parts of water.

Impurities, such as $\mathbf{S}O_2Ho_2$, do not interfere with the reactions.

Sodic Carbonate,* $\mathbf{C}ONao_2$.

Procure the *pure* salt, which should be free from sulphate and chloride. The solution should not give a precipitate, when treated with $\mathbf{N}O_2Ho$ and $\mathbf{Mo}O_2Amo_2$, and should not leave a residue, insoluble in water, on acidulating with pure HCl and evaporating to dryness ($\mathbf{Si}O_2$).

Dissolve the dry salt in five parts of water.

Hydric Disodic Phosphate,* $\mathbf{P}OHoNao_2 + 12Aq.$

Recrystallize the commercial salt and dissolve one part of pure salt in ten parts of water.

Impurities.—Sulphate and Chloride.—Ammonic hydrate should not cause any turbidity on warming (alkaline earthy phosphates).

Sodic Acetate, $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}ONao\end{matrix}\right. + 6aq.$

The commercial salt generally contains sodic sulphate. If a pure salt cannot be procured, sodic acetate may be prepared by neutralizing pure sodic carbonate with pure acetic acid. Dissolve the salt in ten parts of water.

Sodic Acetate and Acetic Acid.

Dissolve 20 grms. of pure crystallized $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}ONao\end{matrix}\right.$ in 160 c.c. of water, and add 40 c.c. of concentrated $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$. This solution is used for the precipitation of ferric, aluminic and chromic phosphates.

Hydric Sodic Sulphite, $\mathbf{S}OHoNao$.

Dissolve one part of the salt in five parts of water. Hydric ammonic sulphite may frequently be used with greater advantage.

Sodic Hyposulphite, $\mathbf{S}SONao_2 + 5aq$.

Readily procurable in a pure state. Dissolve one part of the salt in forty parts of water.

Sodic Hypochlorite, $ClNao$.

Prepared by shaking up one part of bleaching powder, with ten parts of water, and adding a saturated solution of commercial sodic carbonate, as long as a precipitate is produced. Allow to subside, and syphon off.

Ammonic Oxalate,* $\left\{\begin{array}{l}\mathbf{C}OAmo\\ \mathbf{C}OAmo\end{array}\right. + aq$.

Purify the commercial salt by recrystallisation and dissolve one part in 24 parts of water.

Impurities.—The salt should leave no fixed residue on ignition. $\mathbf{S}H_2$ or $\mathbf{S}Am_2$ ought not to produce a turbidity or a precipitate.

Ammonic Carbonate,* $\mathbf{C}OAmo_2$.

Prepared by dissolving one part of the commercial sesquicarbonate, after scraping off from the lumps any foreign matter, in four parts of water and adding one part of strong ammonia solution. If a precipitate of $\mathbf{Fe}_2Ho_6$ be thrown down, it is allowed to subside, and the clear solution is syphoned off.

Impurities.—Iron, lead, sulphuric and hydrochloric acids. The salt should volatilize completely and give no precipitates with $\mathbf{B}aCl_2$ or $\mathbf{N}O_2Ago$ (after acidulating with HCl or $\mathbf{N}O_2Ho$ respectively), also no precipitate with $\mathbf{S}H_2$ or $\mathbf{S}Am_2$.

Hydric Ammonic Carbonate, $\mathbf{C}OHoAmo$.

Obtained in colourless rhombic prisms, on passing $\mathbf{C}O_2$ to supersaturation into a concentrated solution of ammonia. The salt is employed for the separation of $\mathbf{As}_2S_3$ from $\mathbf{Sb}_2S_3$ and $\mathbf{Sn}S_2$. A saturated solution is prepared when required.

Ammonic Chloride,* $AmCl$.

The commercial salt (sal-ammoniac) usually contains iron. Purify by adding to the solution a little ammonic hydrate. Allow the ferric hydrate to subside and neutralize the alkaline filtrate exactly with pure HCl. The salt should leave no fixed residue on ignition. Dissolve in five parts of water.

AMMONIC MOLYBDATE, $\mathbf{Mo}O_2Amo_2$.

This salt may be purchased. It is dissolved in strong ammonia and allowed to stand for some time. A slight yellow precipitate containing ferric hydrate usually subsides. The clear fluid is poured into concentrated $\mathbf{N}O_2Ho$, till the molybdic acid which at first precipitates is entirely redissolved. The nitric acid solution should remain colourless on boiling. A yellow precipitate indicates contamination with $\mathbf{P}OHo_3$, and the reagent should not be used, till it remains clear on digesting.

AMMONIC SULPHATE, $\mathbf{S}O_2Amo_2$.

Recrystallize the commercial salt from an ammoniacal solution in order to separate iron. Keep a saturated solution for use.

AMMONIC NITRATE, $\mathbf{N}O_2Amo$.

The commercial salt is dissolved, when required, to a saturated solution. It should leave no residue when ignited on platinum.

BARIC CHLORIDE,* $\mathbf{Ba}Cl_2 + 2aq$.

The commercial salt is rarely pure enough, and not unfrequently contains lead. It should not give a precipitate with $\mathbf{S}H_2$ or $\mathbf{S}Am_2$, nor should a residue be left after precipitating the whole of the barium by pure $\mathbf{S}O_2Ho_2$ and evaporating the filtrate in a platinum crucible. Purify, if necessary, by passing a current of $\mathbf{S}H_2$, filtering and recrystallizing. Dissolve in ten parts of water.

BARIC NITRATE, $\begin{matrix}\mathbf{N}O_2\\\mathbf{N}O_2\end{matrix}Bao''$.

Should not be precipitated by $\mathbf{N}O_2Ago$, as it is sometimes employed, instead of $\mathbf{Ba}Cl_2$, in order to avoid introducing any chlorine into a solution. Pure baric acetate answers the same purpose. For other impurities, test as for $\mathbf{Ba}Cl_2$. Dissolve one part in 15 parts of water.

BARIC CARBONATE,* $\mathbf{C}OBao''$

Prepared by precipitation of pure $\mathbf{Ba}Cl_2$ with $\mathbf{C}OAmo_2$ and AmHo. Wash well till free from AmCl; stir up the precipitated $\mathbf{C}OBao''$ with water to a thick creamy consistency, and keep it for use in a stoppered bottle. Shake up before using this reagent.

CALCIC CHLORIDE,* $\mathbf{Ca}Cl_2 + 6\ aq$.

The commercial salt is dissolved in five parts of water. The solution should be neutral to test-papers, and should not be precipitated by $\mathbf{S}Am_2$ (iron).

CALCIC SULPHATE, $\mathbf{S}O_2Cao''$.

A saturated solution is prepared by repeatedly shaking up gypsum ($\mathbf{S}OHo_2Cao''$ + aq.) with water, allowing to subside, and syphoning off the clear liquid.

MAGNESIC SULPHATE.

Dissolve the commercial salt ($\mathbf{S}OHo_2Mgo''$ + 6 aq.) (recrystallized, if necessary), in ten parts of water.

FERROUS SULPHATE.

The commercial salt ($\mathbf{S}OHo_2Feo''$ + 6 aq.), is pure enough. Dissolve as required for use in ten parts of water.

FERRIC CHLORIDE,* $\mathbf{Fe}_2Cl_6$.

Prepared by dissolving freshly precipitated and well washed $\mathbf{Fe}_2Ho_6$ in pure HCl, keeping the ferric hydrate in excess. Allow to cool, dilute with an equal bulk of water and filter.

PLUMBIC ACETATE,* $\left(\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}O\end{matrix}\right)_2 Pbo''$.

Dissolve the commercial salt in ten parts of water.

ARGENTIC NITRATE,* $\mathbf{N}O_2Ago$.

Prepared either from silver (pure), or from a silver alloy (a silver coin), by dissolving in pure $\mathbf{N}O_2Ho$, and precipitation as AgCl. Filter off the cupric salt, and wash thoroughly with hot water; transfer to a porcelain dish, and introduce clean strips of zinc. Collect the finely divided silver on a filter, wash thoroughly with hot water, acidulated with a little $\mathbf{S}O_2Ho_2$, and dissolve in $\mathbf{N}O_2Ho$. Evaporate the solution to dryness, and fuse the residue gently. Dissolve in twenty parts of water.

MERCUROUS NITRATE.

Dissolve the crystals of the commercial salt $\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Hg_2o''$ + 2 aq., in 20 parts of cold water, acidulated with 1·2 part of $\mathbf{N}O_2Ho$. Keep some metallic mercury in the filtered solution.

MERCURIC CHLORIDE, $\mathbf{Hg}Cl_2$.

Dissolve the commercial corrosive sublimate in twenty parts of water.

NESSLER'S SOLUTION.

Dissolve 3·5 grms. of KI in 10 c.c. of water; next dissolve 1·6 grm. of $\mathbf{Hg}Cl_2$ in 30 c.c. of water; add the mercury solution gradually, and with continuous agitation to the solution of potassic iodide, until the precipitate ceases to be re-dissolved; then add 60 c.c. of potassic hydrate and filter. Keep in a small bottle out of contact with ammonia.

This reagent is of great value for the detection of mere traces of ammonia.

CUPRIC SULPHATE.

The commercial salt ($\mathbf{S}OHo_2Cuo'' + 4$ aq.) is purified by repeated crystallisation. Dissolve the crystals in ten parts of water.

Impurities.—Iron, zinc.

CUPRIC CHLORIDE, $\mathbf{Cu}Cl_2$.

Prepared by dissolving cupric oxide in HCl.

CUPROUS CHLORIDE, $'\mathbf{Cu}'_2Cl_2$.

Obtained by digesting $\mathbf{Cu}Cl_2$ with metallic copper and HCl.

STANNOUS CHLORIDE, $\mathbf{Sn}Cl_2$.

Prepared by boiling pure granulated tin in concentrated HCl, with the aid of a piece of platinum foil. Dilute with four volumes of water, acidulated with HCl. Keep the filtered solution over granulated tin in a small stoppered bottle.

AURIC CHLORIDE, $\mathbf{Au}Cl_3$.

Prepared by dissolving pure gold in aqua regia, evaporating to dryness on a water-bath, and dissolving in water.

PLATINIC CHLORIDE, $\mathbf{Pt}Cl_4$.

Dissolve some platinum scraps in aqua regia. Precipitate with AmCl. Collect precipitate on a Swedish filter paper; wash with strong alcohol; dry and ignite in a porcelain crucible, gently at first, and lastly to intense redness. Redissolve the spongy platinum in aqua regia. Evaporate repeatedly to dryness on a water-bath, with addition of HCl. Dissolve in ten parts of water. Pure $\mathbf{Pt}Cl_4$ should dissolve completely in pure alcohol.

METALS AND OXIDES.

Zinc, free from arsenic, granulated, and in the form of strips.

Iron (*steel*), *copper*, *tin*, *lead*, *platinum* (used in the form of wire, bars, sheet, turnings) and *mercury* can be obtained of sufficient purity for the purposes of qualitative analysis.

METALLIC LEAD FREE FROM SILVER.

Prepared by precipitation of plumbic acetate by metallic zinc.

PLUMBIC DIOXIDE, $\mathbf{Pb}O_2$.

Readily prepared by digesting red lead, $\mathbf{Pb}_3O_4$, in boiling dilute $\mathbf{N}O_2Ho$. The brown powder is well washed by decantation, and lastly on the filter.

MANGANIC OXIDE, $\mathbf{Mn}O_2$.

Use the powdered commercial black oxide.

HYDRIC PEROXIDE, $\mathbf{O}_2H_2$, OR Ho_2.

A solution may be prepared by passing a current of carbonic anhydride through water in which baric peroxide, $\mathbf{Ba}O_2$, is suspended. The precipitated $\mathbf{C}OBao''$ is filtered off.

Reagents used for Fusions and for Blowpipe Reactions.

SODIC CARBONATE,* $\mathbf{C}ONao_2$.

Should be free from sulphate and chloride.

FUSION MIXTURE* OR WHITE FLUX.

Consisting of dry $\mathbf{C}ONao_2$ and $\mathbf{C}OKo_2$, mixed in the proportion of their combining weights, *i.e.*, 106 + 138, or in the proportion of 10 to 13.

Pure carbonates free from silica, chlorides, and sulphates, should be procured, as their purification cannot be effected without using silver and platinum vessels.

Black Flux.—Prepared by igniting crystals of *Rochelle salt* (potassic sodic tartrate) in a platinum crucible. The residue consists of carbon and alkaline carbonates.

HYDRIC AMMONIC SODIC PHOSPHATE,* $\mathbf{P}OHoAmoNao + 8\ aq.$
(MICROCOSMIC SALT).

The salt should be dried and used in the form of a powder. On being heated in a loop of platinum wire it is converted into $\mathbf{P}O_2Nao$.

POTASSIC CYANIDE,* KCy.

Exceedingly useful for reducing metallic oxides and sulphides, either in the crucible or on charcoal. For blowpipe reactions a mixture of equal parts of KCy and $\mathbf{C}ONao_2$ (or fusion mixture), is preferable, because it sinks readily into the charcoal and yields metallic globules of great purity. The preparation of KCy has been described page 273. For the separation of Ni and Co the salt is dissolved, when required, in twenty parts of cold water, as its aqueous solution is rapidly decomposed.

Potassic Nitrate,* $\mathbf{N}O_2Ko$.

Used as an oxidizing agent. The commercial salt should be purified by dissolving the crystals in hot water to a saturated solution, and allowing to cool in a porcelain dish with continuous stirring. The nitrate falls out first as a fine white powder, and the impurities, *e.g.*, phosphate, sulphate, or chloride are left in the mother liquor.

Potassic Chlorate,* $\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}Ko\end{matrix}\right.$.

This salt can readily be obtained pure, *i.e.*, free from chloride. Either by itself, or in conjunction with HCl, it serves as a powerful oxidizing agent.

Borax,* $\mathbf{B}_4O_5Nao_2 + 10\,aq$.

The crystals should be gently heated in a platinum crucible till the water of crystallisation has been driven off, and the mass kept powdered and ready for use in blowpipe reactions.

Hydric Potassic Sulphate, $\mathbf{S}O_2HoKo$.

Prepared by heating in a platinum crucible 87 parts of $\mathbf{S}O_2Ko_2$ with 49 parts of pure $\mathbf{S}O_2Ho_2$, till the clear mass fuses steadily. Pour out on a porcelain slab, and keep the lumps in a bottle.

Cobaltous Nitrate, $\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Coo''$.

Used in solution only. Should be free from other metals. Dissolve the commercial salt in ten parts of water.

Vegetable Colouring Matters.—Test-papers.

Litmus Solution (comp. p. 117).

Turmeric Paper.—Prepared by digesting at a gentle heat one part of turmeric root with six parts of alcohol. Filter and soak strips of porous paper with the yellow extract. The dried papers should exhibit a fine yellow tint. Like litmus-papers they serve for the detection of free alkalies. All test-papers should be kept in well-stoppered bottles or wooden boxes.

Indigo Solution.—Prepared by gradually stirring four to six parts of *fuming* $\mathbf{S}O_2Ho_2$ into one part of *finely* divided indigo, and allowing the mixture to stand for 48 hours, before pouring it into 20 parts of water. Filter and keep for use in a dark place. The solution of indigo is used for detecting $\mathbf{N}O_2Ho$, $\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}Ho\end{matrix}\right.$, and free chlorine, owing to the formation of products of oxidation of yellow colour.

APPENDIX II.

TABLE SHOWING THE SOLUBILITY OF SALTS IN WATER AND ACIDS.

Names of Salts.	Soluble in Water.	Soluble in or decomposed by Acids.	Insoluble in Water and Acids.
Carbonates	Alkaline carbonates and acid carbonates of Ba, Sr, Ca, Mg, Fe″, Mn, and Pb.	All other carbonates are decomposed by dilute acids, with evolution of $\mathbf{C}O_2$. (Spathose iron ore, and dolomite are decomposed with difficulty.)	None.
Sulphates	Most sulphates, with the exception of those mentioned in Column II and III. ($\mathbf{S}O_2Ago_2$ is difficultly soluble.)	A few basic sulphates, such as of Hg″, 'Hg'$_2$, Fe^{iv}, Bi‴, Sn″.	The sulphates of Ba, Pb, Sr, Ca (Comp. p. 233), and the *red* chromic sulphate.
Sulphites	Alkaline sulphites and the acid sulphites of the alkaline earthy metals.	All other sulphites are decomposed by acids ($\mathbf{C}O_2$ and $\mathbf{B}Ho_3$ excepted), with evolution of $\mathbf{S}O_2$.	None.
Hyposulphites	Most hyposulphites are soluble in water. ($\mathbf{S}SOBao''$, $\mathbf{S}SOAgo_2$, and $\mathbf{S}SOPbo''$ are but little soluble.)	All other hyposulphites are decomposed by acids, with evolution of $\mathbf{S}O_2$ and separation of sulphur.	None.
Sulphides	Alkaline and alkaline earthy sulphides. ($\mathbf{Ca}S$ and $\mathbf{Mg}S$ are only sparingly soluble.)	All other sulphides are decomposed by HCl, with evolution of $\mathbf{S}H_2$, or by $\mathbf{N}O_2Ho$, or aqua regia, with separation of sulphur. (Comp. p. 239.)	None.

Nitrates	Most nitrates, with the exception of a few basic nitrates (Bi, Hg).	A few basic nitrates, which are readily soluble in dilute $\mathbf{N}O_2Ho$.	None.
Nitrites	All nitrites. ($\mathbf{N}OAgo$ is somewhat difficultly soluble.)	—	—
Chlorides	Most chlorides, with the exception of those mentioned in Column III.	[A few oxychlorides.]	The chlorides of Ag, $'Hg'_2$, [Pb] ($\mathbf{Cu}_2Cl_2$, $\mathbf{Au}'Cl$, $\mathbf{Pt}''Cl_2$). (Comp. p. 246.)
Chlorates	All chlorates.	—	—
Hypochlorites	All hypochlorites.	—	—
Bromides	Most bromides, with the exception of those mentioned in Column III.	—	The bromides of Ag, $'Hg'_2$, Pb (less soluble in water than the $\mathbf{Pb}Cl_2$) and of $'Cu'_2$, (soluble in HCl).
Bromates	All bromates.	—	—
Iodides	Most iodides, with the exception of those mentioned in Column III.	$\mathbf{Pb}I_2$, $\mathbf{Hg}I_2$, $\mathbf{Hg}_2I_2$ (decomposed into $\mathbf{Hg}I_2$ and Hg); $\mathbf{Cu}_2I_2$ decomposed by $\mathbf{N}O_2Ho$, with evolution of I.	The iodides of Ag, [$'Hg'_2$, Pb, Hg'', and $'Cu'_2$]. (Comp. p. 256.)
Iodates	The alkaline iodates only dissolve readily in water.	Baric, plumbic, argentic, and other iodates dissolve more or less readily in acids ($\mathbf{N}O_2Ho$).	None.
Fluorides	The alkaline fluorides and a few others, especially AgF, $\mathbf{Hg}F_2$.	The fluorides of the alkaline earthy metals, of lead, and a few other metals.	Fluorspar, decomposed by concentrated $\mathbf{S}O_2Ho_2$ only.

TABLE SHOWING THE SOLUBILITY OF SALTS IN WATER AND ACIDS—*continued.*

Names of Salts.	Soluble in Water.	Soluble in or decomposed by Acids.	Insoluble in Water and Acids.
Silicofluorides	Most silicofluorides are more or less readily soluble in water. The least soluble are those of the alkalies and alkaline earthy metals.	BaF_2, SiF_4 is sparingly soluble in HCl.	None.
Phosphates (ortho-) ..	The alkaline phosphates only.	All other phosphates.	None.
Pyrophosphates	Alkaline pyrophosphates.	All others.	None.
Metaphosphates	The alkaline and a few metallic metaphosphates.	Most others.	—
Silicates	Potassic and sodic silicates are mostly soluble.	Others are decomposed by acids, with separation of $SiHo_4$. All silicates are decomposed by HF.	Many natural silicates. (Comp. p. 269).
Borates	The alkaline borates. All others are difficultly soluble in water, but none are absolutely insoluble.	All borates dissolve in acids.	—
Cyanides	The cyanides of the alkali and alkaline earthy metals, as well as $HgCy_2$.	Most other (single) insoluble cyanides are readily decomposed by acids. (Comp. p. 275.)	AgCy is insoluble in dilute NO_2Ho, but is decomposed by aqua regia.
Ferrocyanides	The alkaline ferrocyanides are readily soluble in water; the alkaline earthy ferrocyanides are difficultly soluble.	Most others are soluble in dilute acids (HCl). (Comp. p. 280.) Prussian blue dissolves in oxalic acid.	Ag_4 $FeCy_6$, insoluble in dilute NO_2Ho, is decomposed by boiling with aqua regia.

Ferricyanides	The alkaline ferricyanides are readily soluble in water. The others are mostly difficultly soluble or insoluble.	Most others are insoluble in dilute HCl.	The ferricyanides insoluble in acids are decomposed by aqua regia. Both ferro- and ferricyanides are decomposed by boiling with KHo. (Comp. p. 281).
Cobalticyanides	Cobalticyanides of K, Na, Ba, Sr, Ca, and Mg are soluble, also the salts of Fe^{iv}, Hg, and Pb.	Most others are insoluble in acids (HCl).	Some (Cu and Ag) are insoluble in acids, but are decomposed by KHo.
Cyanates	The cyanates of the alkalies and alkaline earthy metals, also a few metallic cyanates, are soluble in water.	The few other cyanates which exist are decomposed by dilute NO_2Ho.	—
Sulphocyanates	The sulphocyanates of the alkali and alkaline earthy metals, also of Cu, Hg, Fe^{iv}, are soluble in water.	The few other characteristic sulphocyanates, *e.g.*, of $'Cu'_2$, Ag, $'Hg'_2$, and Pb, are more or less readily decomposed by acids (NO_2Ho).	—
Formates	All formates are soluble in water.	—	—
Acetates	All acetates are soluble in water. (Argentic and mercurous acetates are difficultly soluble.)	—	—
Benzoates	Benzoates of K, Na, Ba, Sr, Ca, Mg, and of Mn, Zn, Fe'', are soluble in water.	Ferric, cupric, argentic, plumbic, and mercurous benzoates are soluble in acids.	—
Succinates	Most succinates are soluble in water.	Succinates of Fe^{iv}, Cu, Ag, Hg, and Pb, dissolve readily in acids.	—

TABLE SHOWING THE SOLUBILITY OF SALTS IN WATER AND ACIDS—*continued.*

Names of Salts.	Soluble in Water.	Soluble in or decomposed by Acids.	Insoluble in Water and Acids.
Oxalates	The alkaline oxalates, as well as of Cr^{iv}, most others are difficultly soluble or insoluble in water.	All other oxalates are soluble in acids.	—
Tartrates	The alkaline tartrates are soluble in water, the acid less so than the normal salts.	The normal tartrates of the alkaline earths, earths and heavy metals are mostly difficultly soluble in water, but dissolve readily in mineral acids (HCl) and in tartaric acid.	—
Citrates	The alkaline citrates are soluble in water; most others are insoluble, or difficultly soluble.	Citrates insoluble in water dissolve readily in acids.	—
Arseniates and Arsenites ..	The alkaline arseniates and arsenites are soluble in water; most others are insoluble.	Arseniates and arsenites insoluble in water, dissolve in acids, and frequently also in ammonic salts.	None.
Chromates	The chromates of the alkalies, as well as of Sr, Ca, Mg, are soluble in water. Most others are insoluble.	All chromates insoluble in water dissolve in acids (in HCl, with evolution of chlorine, and in SO_2Ho_2, with liberation of oxygen).	Ignited plumbic chromate.

APPENDIX III

(A.) EXAMINATION OF A SIMPLE SALT.

Preliminary Examination for Base.

Substance given: white crystalline, readily soluble in water, reaction of solution alkaline.

Experiment.	Observation.	Inference.
Heated some of the powdered substance in a dry test-tube.	Gave off water; fused; was slightly blackened; gave off CO, burning with a blue flame.	Oxalate, formate.
Treated residue with water, and filtered. Tested with litmus paper.	The residue dissolved; the solution reacted strongly alkaline.	
Added dilute HCl	Effervescence, whilst before ignition the substance did not effervesce.	Alkaline oxalate.
Tested HCl extract on platinum wire in a Bunsen's gas flame.	Violet flame	Potassium.

Examination of Solution for Base.

Added HCl.				
No precipitate. Absence of Group I.	Added a solution of $\mathbf{S}H_2$ to the same solution.			
	No precipitate. Absence of Group II.	To a *fresh* portion of the solution added AmCl, AmHo, and $\mathbf{S}Am_2$.		
		No precipitate. Absence of Group III.	To the same solution added $\mathbf{C}OAmo_2$.	
			No precipitate. Absence of Group IV.	The solution may contain— $\mathbf{Mg}O$, $\mathbf{O}K_2$, $\mathbf{O}Na_2$. Tested a fresh portion of solution specially for K by adding HCl and $\mathbf{Pt}Cl_4$, *yellow crystalline* precipitate. **Presence of K.**

Preliminary Examination for Acid.

Experiment.	Observation.	Inference.
Treated a portion of the powdered substance with concentrated $\mathbf{S}O_2Ho_2$.	CO and $\mathbf{C}O_2$ given off, with slight blackening of substance.	
Passed gas into lime-water and applied a light to the unabsorbed gas.	White precipitate in lime-water; gas burnt with blue flame.	From decomposition of oxalate.

EXAMINATION OF SOLUTION FOR ACID.

Acidulated with HCl.	Acidulated with $\mathbf{N}O_2Ho$.	Acidulated with $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$.	
No precipitates.	No precipitates.	$\mathbf{Ca}Cl_2$, a white precipitate. $\mathbf{S}O_2Cao''$ ditto. Presence of $\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right.$.	
Found **Potassic Oxalate.**			

(B.) EXAMINATION OF A COMPOUND SUBSTANCE.

PRELIMINARY EXAMINATION FOR BASES.

Compound given: a dirty white powder.

Experiment.	Observation.	Inference.
Heated some of the powdered substance in a dry test-tube.	Substance fused and gave off heavy white fumes, which condensed in the upper part of the tube.	Compounds of Am, Hg, As, etc.
	Gave off reddish-brown fumes and a gas which supported combustion. The residue was yellowish whilst hot, dirty white on cooling.	From decomposition of nitrates, such as of Pb, Bi, etc.

PRELIMINARY EXAMINATION FOR BASES—*continued*.

Experiment.	Observation.	Inference.
Heated a portion of the substance mixed with $\mathbf{C}ONao_2$ in a bulb-tube.	$\mathbf{N}H_3$ given off. Mirror and metallic globules.	Am and Hg compounds.
Heated some of the powdered substance on charcoal before the blowpipe flame.	Substance gave off heavy fumes, and was partly reduced to the metallic state. The metal was malleable; the incrustation yellow. A portion of the ignited mass appeared strongly luminous.	Pb. Alkaline earthy bases.

EXAMINATION OF SOLUTION FOR BASES.

Substance dissolved partly in water, partly in HCl, with evolution of $\mathbf{C}O_2$. On mixing the two solutions, acicular crystals of $\mathbf{Pb}Cl_2$ fell out. Filtered off. Confirmed presence of lead by means of $\mathbf{Cr}O_2Ko_2$ or $\mathbf{S}O_2Ho_2$.

<table>
<tr><td colspan="4">Passed a current of $\mathbf{S}H_2$.</td></tr>
<tr><td rowspan="4">A black precipitate.</td><td colspan="3">Evaporated filtrate to dryness, with a few drops of $\mathbf{N}O_2Ho$. Took up with water. Added AmCl, AmHo, and $\mathbf{S}Am_2$.</td></tr>
<tr><td rowspan="2">No precipitate.
Absence of Group III.</td><td colspan="2">To the same solution added $\mathbf{C}OAmo_2$.</td></tr>
<tr><td>A white precipitate.</td><td>On evaporating filtrate to dryness, and igniting, no fixed residue was left.
Absence of Mg, K, Na.</td></tr>
</table>

EXAMINATION OF PRECIPITATE PRODUCED IN GROUP II.

<table>
<tr><th colspan="4">Washed precipitate till free from HCl, and boiled with $\mathbf{S}Am_2$.</th></tr>
<tr><td colspan="3">Residue.—Boiled with $\mathbf{N}O_2Ho$. Diluted with $\mathbf{O}H_2$, and added dilute $\mathbf{S}O_2Ho_2$ and methylated spirit. Filtered.</td><td rowspan="3">Solution.—Acidulated with dilute HCl. No yellow precipitate. Absence of As, Sb, and Sn.</td></tr>
<tr><td colspan="2">Residue.—Boiled in ammonic acetate, and filtered.</td><td rowspan="2">Solution.—$\mathbf{S}H_2$ added to a portion of solution gave no precipitate. Absence of Bi, Cu, Cd.</td></tr>
<tr><td>Residue.—Dried and ignited in a bulb-tube, with dry $\mathbf{C}ONao_2$. Metallic mirror and globules. Presence of Hg.</td><td>Solution.—Added $\mathbf{Cr}O_2Ko_2$, yellow precipitate. Presence of Pb.</td></tr>
</table>

EXAMINATION OF PRECIPITATE PRODUCED IN GROUP IV.

Dissolved precipitate in a little dilute HCl. Tested a portion of the solution with $\mathbf{S}O_2Cao''$—no precipitate, even after some time. **Absence of Ba and Sr.** Confirmed presence of Ca by adding to another portion of the solution AmHo and $\left\{\begin{matrix}\mathbf{C}OAmo\\ \mathbf{C}OAmo\end{matrix}\right.$. A white precipitate. **Presence of Ca.**

PRELIMINARY EXAMINATION FOR ACIDS.

Experiment.	Observation.	Inference.
Treated with dilute HCl.	Effervescence. The gas precipitated lime-water.	$\mathbf{C}O_2$.
Treated with concentrated $\mathbf{S}O_2Ho_2$.	Cl and nitrous fumes.	HCl and $\mathbf{N}O_2Ho$.
Confirmed HCl by heating substance with $\mathbf{Mn}O_2$ and $\mathbf{S}O_2Ho_2$.	Chlorine evolved.	HCl.
Ditto $\mathbf{N}O_2Ho$ by means of $\mathbf{S}O_2Ho_2$ and $\mathbf{S}O_2Feo''$.	A brown ring was formed.	$\mathbf{N}O_2Ho$.

EXAMINATION OF SOLUTION FOR ACIDS.

Prepared solution by boiling some of the powder with a solution of $\mathbf{C}ONao_2$; filtered, and acidulated with—

HCl.	$\mathbf{N}O_2Ho$.	$\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$.	Neutral solution.
No precipitates.	$\mathbf{N}O_2Ago$, white curdy precipitate, soluble in AmHo. **Presence of HCl.**	No precipitates.	No precipitates.

Found—Bases: $\mathbf{Hg}O$, $\mathbf{Pb}O$, $\mathbf{Ca}O$, $\mathbf{O}Am_2$.
Acids: $\mathbf{C}O_2$, $\mathbf{N}O_2Ho$, HCl.

APPENDIX IV.

The following Tables, published by Messrs. De la Rue and Co., will enable the student to convert French weights and measures based upon the decimal system into their English equivalents:—

French Measures of Length.

	In English inches.	In English feet = 12 inches.	In English yards = 3 feet.	In English fathoms = 6 feet.	In English miles = 1760 yards.
Millimètre	0·03937	0·003281	0·0010936	0·0005468	0·0000006
Centimètre	0·39371	0·032809	0·0109363	0·0054682	0·0000062
Décimètre	3·93708	0·328090	0·1093633	0·0546816	0·0000621
Mètre	39·37079	3·280899	1·0936331	0·5468165	0·0006214
Décamètre	393·70790	32·808992	10 9363310	5·4681655	0·0062138
Hectomètre..	3937·07900	328·089920	109·3633100	54·6816550	0·0621382
Kilomètre	39370·79000	3280·899200	1093·6331000	546·8165500	0·6213824
Myriomètre	393707·90000	32808·992000	10936·3310000	5468·1655000	6·2138244

1 inch = 2·539954 centimètres.
1 foot = 3·0479449 décimètres.

1 yard = 0·9143835 mètre.
1 mile = 1·6093149 kilomètre.

French Measures of Surface.

	In English square feet.	In English square yards, = 9 square feet.	In English poles = 272·25 square feet.	In English roods = 10890 square feet.	In English acres = 43560 square feet.
Centiare, or square mètre	10·764299	1·196033	0·0395383	0·0009885	0·0002471
Are, or 100 square mètres	1076·429934	119·603326	3·9538290	0·0988457	0·0247114
Hectare, or 10,000 square mètres	107642·993418	11960·332602	395·3828959	9·8845724	2·4711431

1 square inch = 6·4513669 square centimètres.
1 square foot = 9·2899683 square décimètres.
1 square yard = 0·83609715 square mètre or centiare.
1 acre = 0·40467102 hectare.

FRENCH MEASURES OF CAPACITY.

	In cubic inches.	In cubic feet = 1728 cubic inches.	In pints 34·65923 cubic inches.	In gallons = 8 pints = 277·27384 cubic inches.	In bushels = 8 gallons = 2218·19075 cubic inches.
Millilitre, or cubic centimètre	0·06103	0·000035	0·00176	0·0002201	0·0000275
Centilitre, or 10 cubic centimètres ..	0·61027	0·000353	0·01761	0·0022010	0·0002751
Décilitre, or 100 cubic centimètres ..	6·10271	0·003532	0·17608	0·0220097	0·0027512
Litre, or cubic décimètre	61·02705	0·035317	1·76077	0·2200967	0·0275121
Décalitre, or centistère	610·27052	0·353166	17·60773	2·2009668	0·2751208
Hectolitre, or décistère	6102·70515	3·531658	176·07734	22·0096677	2·7512085
Kilolitre, or Stère, or cubic mètre ..	61027·05152	35·316581	1760·77341	220·0966767	27·5120846
Myriolitre, or decastère	610270·51519	353·165807	17607·73414	2200·9667675	275·1208459

1 cubic inch = 16·386176 cubic centimètres.
1 cubic foot = 28·315312 cubic décimètres, or litres.
1 gallon = 4·543358 litres.

French Measures of Weight.

	In English grains.	In troy ounces = 480 grains.	In avoirdupois lbs. = 7000 grains.	In cwts. = 112 lbs. = 784000 grains.	Tons = 20 cwts. = 15680000 grains.
Milligramme	0·01543	0·000032	0·0000022	0·0000000	0·0000000
Centigramme	0·15432	0·000322	0·0000220	0·0000002	0·0000000
Décigramme	1·54323	0·003215	0·0002205	0·0000020	0·0000001
Gramme	15·43235	0·032151	0·0022046	0·0000197	0·0000010
Décagramme	154·32349	0·321507	0·0220462	0·0001968	0·0000098
Hectogramme	1543·23488	3·215073	0·2204621	0·0019684	0·0000984
Kilogramme	15432·34880	32·150727	2·2046213	0·0196841	0·0009842
Myriogramme	154323·48800	321·507267	22·0462126	0·1968412	0·0098421

1 grain = 0·064799 gramme.
1 troy oz. = 31·103496 grammes.

1 lb. avoir. = 0·453593 kilogr.
1 cwt. = 50·802377 kilogrs.

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